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Rock phosphates and other mineral fertilisers: their origin, value, and sources of supply.

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ROCK PHOSPHATES

AND OTHER

MINERAL FERTILISERS:

THEIR

ORIGIN, VALUE, AND SOURCES OF SUPPLY.

BY

CHARLES CHEWINGS,

PH.D., F.G.S., F.R.G.S., M.D.G.G., M.I.M. AND M.E., ETC.

WITH MAP OF THE CLINTON DEPOSIT.

South Australia:

C. E. BRISTOW, GOVERNMENT PRINTER, NORTH TERRACE, ADELAIDE.

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PREFACE.

THE need of some concise description of the sources of supply of mineral fertilisers has, to my mind, been apparent for some time past; in fact, this pamphlet is the outcome, in the first place, of notes taken while looking up the literature on phosphate deposits. Reliable descriptions of the deposits and material from which mineral fertilisers originate, and their modes of occurrence, should prove useful to the prospector, and for this reason several *verbatim* descriptions by different authors have been inserted. In a work of this kind, covering, as it does, so much ground, one is, of necessity, under obligation to many workers. The observations of any one person, however capable and industrious, would be a very incomplete record. Various opinions are expressed on one and the same deposit, and the necessity devolves upon the author to sift the evidence and strike as near to the true version as is possible. References to various authors will be found in the text. In any partially explored and exploited country such information as is herein afforded should not only have an interest for those who use fertilisers, but be of value to everyone who travels about with eyes open, if only for comparison, for the discovery of similar deposits to those described may mean a fortune to the discoverer. Up-to-date statistics are not available, but the latest obtainable are given. Some idea of the magnitude and commercial importance of the industries will be apparent from the statistics, and the descriptions of the deposits will show the intelligent prospector where and for what to look for similar occurrences.

There is no apparent reason why rock phosphate deposits, nitrate deposits, or potash and salt beds, other than those already discovered, should not exist in Australia. Nature, for some unaccountable reason, often places her best treasures in localities that are hopelessly barren for other purposes. It is impossible to say what value may lie beneath the surface in those flat areas of slight elevation that stretch inland from the coast until they have been prospected.

The percentages given in the descriptions will be a guide as to what should be payable material. The current market price per unit can always be obtained from local manufacturers of the marketable products. Scientific terms have been avoided where possible, though to make

meaning clear without much circumlocution these could not be wholly avoided. and I have thought it desirable to insert chemical formulas and equations, for to those who understand them they convey a clearer meaning than words. My object in writing those parts that have direct reference to agriculture, horticulture, &c., has been to afford those who are practically engaged in the use of the products made from the deposits described the benefit of my researches, both theoretical and practical; to some they may be the means to a better understanding of, and the uses to which, the fertilisers may be applied. Since mineral fertilisers have been systematically used in South Australia the commercial aspect of agriculture, as an industry, has obtained a new lease of life, and land has, in some parts, increased in value from £1 to £2 per acre, solely through making the land more prolific. When these are more extensively used, as experience coupled with good judgment will dictate, there is no doubt that still more satisfactory results will be obtained. The amount of farmyard manures cannot supply the annual loss to the land from the crops grown, and if the land is to continue profitable an artificial supply must be restored to it.

During the compiling of this little book the object of supplying only useful information and material for comparison has ever been prominent in my mind, and if the information afforded should be the means of helping anxious inquirers to a better knowledge of the subject I shall feel gratified and amply repaid for the time and trouble it has cost me.

CHAS. CHEWINGS.

Adelaide, October 1st, 1902.

Rock Phosphates and other Mineral Fertilisers:

Their Origin, Value, and Sources of Supply.

I. INTRODUCTION.

There is no question connected with agriculture which is of greater direct and practical importance, particularly in those countries which have been depleted of their active fertility, than definite knowledge of the true principles which govern the profitable use of common fertilisers. (Voorhees.)

As every one knows, the chief function of manures is to supply something lacking in the soil essential to plant life. As a rule it is nitrogen, potash, or phosphoric acid. Sandy soils, unless derived direct from granitic rocks, as a rule lack potash. Clays, on the other hand, are frequently rich in potash, but may be deficient in lime and phosphoric acid. Limestone soils are frequently rich in phosphates as they may be poor in potash and nitrogen. Soils such as peaty swamps, which owe their origin to accumulations of decaying vegetation, are usually rich in nitrogen and poor in all other essential mineral constituents. It may be accepted as an axiom that the soil must contain the elements contained in the plant. The removal by constant cropping partially exhausts even fertile soils of these essentials. The elements—nitrogen, potassium, phosphorus, magnesium, sulphur, sodium, iron, chlorine, silicon, and calcium—are all found in plants, but the three most liable to exhaustion are nitrogen, potash (potassium), and phosphoric acid (phosphorus), to which one other, in certain cases, perhaps should be added, viz., lime (calcium), because they exist in larger amounts than the others in the plants that are grown, and in smaller amounts than the others in even the most fertile soils. Nitrogen measures the crop-producing power or fertility of a soil, for without it good crops cannot be grown, even when potash and phosphoric acid are abundant. No other element can substitute the nitrogen required by the plant, and if absent from the soil the plant suffers. Water, climate, and season facilitate good crops, but these alone will not produce them. Water is essential for the solution of the food elements in the soil, as well as for their distribution in the plant after they have been acquired. Given the fertile element in a soil, the climatic and seasonal conditions exert an important influence on its productive powers. Soils that are naturally poor, or have become partially exhausted of their plant food elements, must have those elements that are lacking supplied in proper quantity, or good crops cannot be grown. It is therefore important first to know the chemical

composition of the soil to be able to judge which element it lacks, and, secondly, to remember which elements are being used up by constant cropping; otherwise it may be that wrong or unnecessary manures are being applied. Nitrogen is the most expensive of the three essentials to apply, and being the most soluble it is liable to be carried off in rain waters. To-day, as happily stated by Voorhees, it is an element of the atmosphere, to-morrow a constituent of a growing plant, the next day as an animal product, and the day following it may be returned to the soil to feed the plant. In the nitrate form nitrogen remains freely movable, and it has been found that vegetable matter (humus) in the soil and thorough tilling of the soil prevents, to some extent, the loss of nitrogen by drainage. Continuous wheat and corn growing is responsible for losses in this expensive element of fertility, and should be alternated with crops of clover, field peas, or some such plants. The phosphoric acid in mineral superphoshates readily becomes chemically "fixed" in the soil (and is not so readily removed by rain waters as is nitrogen), and the same is the case with potash, but, on the other hand, they are not naturally returned to the soil, as is the case with nitrogen when land lies fallow by absorption from the air. The tendency of phosphates is to revert to their original and insoluble form, but nitrates do not combine to make insoluble compounds, but remain freely soluble; hence good judgment is required both as to amount and method of application. Leguminosæ, *e.g.*, clovers, peas, beans, vetches, &c., possess the property of acquiring nitrogen direct from the air. Farm crops, on the contrary, obtain their supplies, largely or wholly, from the soil.

II.—SOURCES OF NITROGEN IN FERTILISERS.

Decaying Vegetable Matter produces ammonia, from which nitrate is formed, and in this form the roots of plants can absorb and assimilate the nitrogen it contains. The able paper read before the Royal Society some time back by Professor Rennie, of the Adelaide University, throws much light on the process nature adopts in this connection.

Guano also contains nitrogen. The excrement of birds and bats originates such deposits, the chemical combinations of which are sometimes very complicated; but the nitrogen contained is "available," and wonderful results are often obtained from its application. Peru and the islands off its coast formerly supplied the largest quantity and the richest deposits. The three small but famous Chincha Islands yielded over 10,000,000 tons of guano. Other guano deposits exist further north on the South American coast, but they are not so rich as the Peruvian; also on islands on the south-west coast of Africa, and many other places. Bat guano occurs in caves in Mexico and in some of the south-western States of America. The Chincha deposits were sometimes 100ft. to 200ft. in depth, and rested on granite. Pelicans, penguins, and sea gulls are the depositors. The richest guanos contained 20 per cent. of nitrogen; the poorer yielded 9 per cent. to 11 per cent. Most of the nitrogen is present as uric acid and ammonia; 14 per cent. of nitrogen would represent 17 per cent. of ammonia. The damp guanos carry the

nitrogen in the form of ammonia principally. "Equalised or rectified" guanos contain, first quality, 8 per cent. to 9 per cent. of ammonia, 30 per cent. to 35 per cent. phosphate, and 2 per cent. to 3 per cent. of potash; the second quality contains half as much nitrogen, but more phosphate. Guano and salt mixed together are said to yield excellent results, the salt seeming to be beneficial to the guano. There are artificial products, such as *meat meal guano*, which contains 4 per cent. to 8 per cent. of nitrogen and 13 per cent. to 20 per cent. of phosphoric acid; and *fish guano* contains 8 per cent. to 10 per cent. of nitrogen and 4 per cent. to 15 per cent. of phosphoric acid. *Bat guano* contains 9 per cent. of nitrogen and 25 per cent. of phosphoric acid. Guano is extremely light, and its ash is soluble in water; when an insoluble ash occurs it is impure.

Sulphate of Ammonia is a chemical salt which (according to Voorhees), when pure, contains 21·2 per cent. of nitrogen (other authorities give 24½ per cent.). In commercial forms, however, it usually contains about 20 per cent. (others give 24·5 per cent. as the selling basis), and even this makes it the richest in nitrogen of any of the commercial nitrogenous products; that is, every ton contains 400lbs. of nitrogen, and is thus richer by 60lbs. per ton than nitrate of soda, the next highest grade of nitrogenous products. Sulphate of ammonia is obtained from the dry distillation of animal bone in the manufacture of bone-black, from the distillation of coal in the manufacture of illuminating gas, and from coal in the manufacture of coke. It is quick to act, thus making it a very useful form, especially for quick-growing crops. One hundred pounds to 125lbs. per acre is a good dressing, and it is best sown alone. Its physical structure is such as to permit its ready distribution in a mixture.

Nitrate of Soda.—Vast deposits of this mineral are found in the rainless districts of South America. These crude salts contain from 4 per cent. to 10 per cent. of nitrogen, and are dissolved and recrystallised to remove impurities before they are put upon the market. The chemically pure salt nitrate of soda contains 16·47 per cent. of nitrogen, and the commercial article called "Chili saltpetre" contains from 15·5 per cent. to 16 per cent. Dana says that in the district of Tarapaca, Northern Chili, and also in the neighboring parts of Bolivia, the dry pampa lands, for forty leagues, at a height of 3,300ft. above the sea, are covered with beds of this salt, (caliche) soda nitre, several feet in thickness, along with gypsum, common salt, glauber salt, and remains of recent shells. These nitrate deposits are of great commercial value. They formerly belonged to Peru, but passed into the hands of Chili in 1884. The nitrate is frequently found covered by layers of other earthy material. Holes are sunk, and large quantities are blown out with powder; the nitrate is then collected and treated. One writer estimated there were 100,000,000 tons to work on. About a million tons are taken out yearly. Arkman puts the life of the deposit at thirty-five years.

Russell states ("Nitrate Fields of Chile," p. 290) that the nitrate of soda, or "caliche," may be snow-white, sulphur, lemon, orange, violet, blue, and sometimes brown, like raw sugar; it generally contains 30 per cent. to 35 per cent. pure nitrate of soda, also 25 per cent. to 40 per cent It

is crushed by rollers and dissolved by "systematic lixiviation," similar to the method used in the manufacture of soda. Common salt is the commonest impurity; gypsum, sulphate of potassium, sodium, and magnesium, along with insoluble matter, are the other impurities. Iodine is also extracted at these "oficinas." Commercial nitrate of soda contains 95 per cent. of pure nitrate of soda, or about 15½ per cent. of nitrogen, which, if calculated as ammonia, would be 19 per cent. The annual export value has been estimated at six millions to seven millions sterling. Nitrate of soda is used also for the manufacture of nitric and sulphuric acid, and also saltpetre, the chief constituent of gunpowder. The "salinas" yield also salts of lime, soda, alumina, magnesia, and boracic acid. The latter has its source probably from volcanoes, while all the others may be derived from the evaporation of sea water and its action on the adjoining rocks. Nitrate of soda is very soluble, and is mostly used as a top dressing. As it is costly, it can be sown with common salt with advantage. It should not be mixed with common salt long before sowing, as a chemical change takes place in which the nitrogen will be partly lost, viz., the nitric acid in the nitrate of soda. Nitrate of soda contains its nitrogen as nitric acid—the most valuable and readily assimilable form, and the form into which all other forms of nitrogen have first to be converted. Nitrate of soda is the cheapest form of nitrogenous manure. It must be used with discretion, viz., 1cwt. to 2cwts. per acre. Its benefits last only for one year, and several doses are better than one.

Nitrogen is the most expensive constituent of fertilisers, and, all things considered, is one of the most useful. Its production and application to soils by means of green soiling, animal manures, cotton-seed meal, &c., need not be dealt with here. In the form of nitrate plants can take up the nitrogen immediately. Ammonia will change to a nitrate rapidly, and appears to be quite as useful in many ways. Like the nitrate, it is soluble in water, and thus readily distributes itself through the surface soil. Deposits also occur in Humboldt County, Nevada, United States of America, also in California, and is reported from Southern New Mexico.

Nitrates, according to Vacher, possess the following characteristics:—Soluble in water; undergo decomposition at an intense red heat. Thrown on red-hot charcoal, deflagration takes place; *i.e.*, the charcoal burns at the expense of the oxygen in the nitric acid, with vivid scintillation. A nitrate mixed with cyanide of potassium, in powder, and heated in small quantity on platinum foil, deflagrates vividly, accompanied by ignition and detonation. Nitrate mixed with copper filings and heated in a test tube with concentrated sulphuric acid yields a yellowish-red tint. The coloration may be better observed by looking lengthwise through the tube. (The yellowish tint is due to the nitric oxide, which is liberated upon the oxidation of the copper by the nitric acid combining with the oxygen of the air to hyponitric acid.) If a little brucia is dissolved in concentrated sulphuric acid and a small quantity of a fluid containing nitric acid is added to the solution the latter immediately acquires a magnificent red color; the color soon passes into reddish-yellow. Chloric acid gives the same reaction. Nitrates heated in a piece of hard glass

tubing, closed at one end, gives off reddish-brown fumes (= nitrogen tetroxide NO_2); or, if when heated together with bisulphate of potash, in a tube closed at one end, red fumes with a smell of nitrous acid are given off, the reaction indicates the presence of nitric or nitrous acid.

III.—SOURCES OF POTASH IN FERTILISERS.

Potash manure, such as the muriate, sulphate, and carbonate of potash, through the form in which it is combined, exerts less influence upon the availability of the elements to the plant than is the case with nitrogen and phosphoric acid. All of these forms are soluble and can be readily absorbed. The chemical form or combination of the potash salts seem to exert but relatively little influence upon the "availability" of the constituent—whether in the form of a muriate or chloride, a sulphate or a carbonate—notwithstanding that there is a difference in the rate at which they will distribute in the soil before becoming fixed. Chloride (or muriate), however, has been found to be deleterious to the tobacco plant.

The *Muriate of Potash* is more generally used than any of the other manufactured products, and contains about 50 per cent. of actual potash, equivalent to 80 per cent. muriate. In all cases this form of potash is sold upon the basis of 80 per cent. muriate. A Scotch product runs as high as 98 per cent. of pure muriate.

High-grade Sulphate of Potash is usually sold on a purity basis of 98 per cent., or an equivalent of 53 per cent. actual potash. It is rather less diffusible than the muriate, though it is not believed to be inferior to it as a source of actual potash. There is also *a double sulphate of potash* and magnesia in the market, with a 26 per cent. of actual potash content.

Upon standing, all the potash salts have a tendency to become hard, though, with the exception of kainit, they are easily pulverised, and thus readily distributed, either broadcast or in drills. Potash, like phosphoric acid, is readily "fixed" in the soil. Heavy applications of muriate of potash may result in the exhaustion of lime in the soil by the chlorine combining with lime or soda, forming soluble chlorides of lime or soda, and being washed away by rain waters.

The celebrated Stassfurth beds, in North Germany, supply nearly all the potash for artificial manure. These beds are of immense commercial value, and are supposed to have originated in a somewhat similar way to the nitrate of soda beds in Chile, viz., from the evaporation of sea water; but they are, geologically, much older, being of Permian age. (Zechstein.) Kayser states that the beds are known at Stassfurth, Egeln, Vienenburg, and other places north of the Hartz Mountains, and that the beds are of great thickness. The salt-bearing beds are over 1,200ft. thick, over which—and 150ft. thick—is a zone in which potash and magnesian minerals occur, called abraum salts, such as polyhalite, kieserite, carnallite, and kainite. The carnallite is the chief source of the potash as a manure. Kainite is the name of a potash manure in the market. The commercial articles are specially prepared from these, and are exported to all parts of the world in large quantities. Salt, in

immense quantity, occurs in the same beds, and also gypsum. Both the salt and potash minerals are said to occur in such quantity and to extend over such large areas as to be practically inexhaustible. The beds come to the surface, but also plunge beneath tertiary and other rocks to considerable depths. Bischof has drawn a section which shows the beds in undulations. The lowest are the salt layers, which repose on so-called stinkshiefer of Zechstein age; next the potash layers; above this are salt clay beds, followed by gypsum beds, also of Zechstein age. Buntersandstein follows on and is overlain by tertiary and diluvium beds. At Sperenberg, seven miles south of Berlin, the beds were proven by boring to be several thousands of feet thick.

The principal potash-bearing minerals (or potassium salts) from which the potash for manure is obtained are—

Polyhalite	$= 2CaSO_4, MgSO_4, K_2SO_4 + 2H_2O$, carrying	15·6 %	of potash.
Kainite	$= MgSO_4, KCl + 3H_2O$	" 18·9	"
Carnallite	$= KCl, MgCl_2 + 6H_2O$	" 14·1	"
Picromerite	$= MgSO_4, K_2SO_4 + 6H_2O$	" 23·4	"
Sylvite	$= KCl$ (has the form and taste of common salt)	52·4	"

They may be looked for in the same beds with such minerals as kieserite, $MgSO_4 + H_2O$; gypsum, $CaSO_4 + 2H_2O$; anhydrite, $CaSO_4$; halite (= common salt), $NaCl$; and calcite, $CaCO_3$; in or on clay, marl, or sandstone beds of any geological age. Saline beds occur in most desert or semi-desert regions. The above potash-bearing minerals are all more or less soluble in water, are all very soft, like rock salt or gypsum, and range from colorless through white, bluish, brown, yellowish, to reddish, flesh red, and deep red; the color in most cases being due to some metallic oxide or acid. Occasionally they occur in crystalline form, showing perfect cleavage and characteristic lustre, but more commonly they are found in granular masses, which may or may not be crystalline, or in beds which sometimes are of considerable thickness; also massive, and as incrustations.

A technical description of each species may be found in Dana's "Mineralogy," 6th edition, but samples had better be submitted to competent authority for identification. The following tests, however, may prove useful:—

(1) A solution of tartaric acid added in excess to a moderately strong solution of potassium salt gives, after some time, a white crystalline precipitate of cream of tartar; the effect is greatly promoted by strong agitation.

(2) Potassium salts usually color the outer blow-pipe flame purple or violet; this reaction is clearly perceptible only when the potassium salts are pure. (Fownes.)

J. Launder's Blow-pipe Test for Potassium is as follows:—Potassium salts held in the non-luminous flame by clean platinum forceps eventually, after moistening with hydrochloric or sulphuric acid, colors the flame violet; when seen through blue glass the color appears reddish-violet, and through green glass bluish-green.

If the colors, after moistening of the material with sulphuric acid for a short time, are orange, invisible or weak, and orange-yellow respectively,

the reduction indicates soda; or if orange, reddish-violet, and orange-yellow respectively, potassium and soda are indicated.

In Reference to the Origin of Potash.—Minerals from which the potash in manures is obtained are of secondary origin. The felspars and micas in certain granites and other rocks of similar origin, as well as the glassy matrix and pumiceous ejectamenta of some volcanoes, contain large percentages of potash. Carbonic and other acids decompose these, and the potash therein is carried, in solution, to lower levels. As potash readily fixes itself in the soil part is detained on the way, but a large proportion is carried into lakes and into the sea, where it is held in solution until the conditions are favorable for precipitation. Other minerals yield lime, soda, magnesia, &c., in the same way. The Great Salt Lake of North America contains immense quantities of sodium sulphate in solution; the waters of the Dead Sea and numerous other lakes contain high percentages of salt; others contain preponderating percentages of borax, gypsum, and the ingredients of very many other minerals. Where the sea is receding along flat rising coasts barriers of sand are formed which, in times of storm, the sea washes over into lagoons and is evaporated, and the salts are precipitated and form beds of salt, gypsum, &c., &c. The same thing occurs with saline lakes that are drying up. In this connection the remarks of F. Bischof, and quoted by Dana, are important. He divides the Strassfurth salt beds vertically into four regions, corresponding, he observes, to the natural order of origin from an evaporating saline —(1) or lower, the *anhydrite* region; (2) the *polyhalite;* (3) the *kieserite;* and (4) the *carnallite.* The kieserite is in beds 9in. to 12in. thick alternating with common salt. The whole deposit is 190ft. thick and has the following as its mean percentage-composition: Common salt, 65; kieserite, 17; carnallite, 13; magnesium chloride (hydrated), 3; anhydrite, 2 = 100.

IV.—THE ORIGIN OF PHOSPHATE DEPOSITS.

The sources from which phosphoric acid in fertilisers is derived will now be briefly described. In order that a clear understanding of the origin of such deposits may be arrived at the descriptions will be preceded by some remarks bearing on the question. The fact that rock phosphates have been found recently both in Australia and New Zealand renders any excuse for particularising this branch of the subject unnecessary. A reference to the statistics that follow will soon convince sceptics that a really good phosphate deposit is as good as a gold mine. Both in Australia and New Zealand there is every likelihood that extensions of the already discovered beds will be found by careful search, and there is always the possibility of other deposits being found. Phosphate rock can so easily be mistaken for common forms of limestone that the writer has ventured to include again and again close descriptions of the different forms phosphate rock assumes. When it is remembered that the phosphate rock deposit at Clinton, South Australia, remained undiscovered for many years, notwithstanding that the surface of the land was tilled, ironstone quarries were opened on it, and that loose blocks of the rock were brought to the surface by the plough, or that a face of the rock

had been exposed in a limestone quarry at Clarendon, New Zealand, for several years without being noticed, it seems desirable that its modes of occurrence should be well understood; and the writer hopes that persons interested will find what they need in this respect in the following pages.

Dr. Wyatt's book, "Phosphates of America," published in 1894, is a valuable contribution to the literature on phosphates. In sketching the history of the deposits he says—"With the fall of temperature on the cooling of the earth's crust certain vapors condensed into acid bodies. These attacked the alkaline crust and combined with its most powerful bases to form salts, *e.g.*, sulphate of lime, which were deposited, while chlorides remained in solution in the seas. When the stronger acids were neutralised the weaker carbonic acid came into play. Carbonic acid is probably the most important factor we have to reckon with in the chemical world to-day. Its union with lime is everywhere before us in common limestones. Its action on other rocks has decomposed them, and the product has produced the fertile soils containing silicates of aluminium, potassium, sodium, magnesium, and iron; also phosphates, sulphates, and chlorides—sandy, clayey, and limy soils."

Bone phosphate, tribasic phosphate of lime, and tricalcic phosphate are synonymous terms for a definite chemical compound. This substance is contained in a mineral called "apatite" or a rock variously called "rock phosphate," "phosphate," "pebble rock," &c., &c. This phosphate rock is the principal source of the phosphoric acid contained in superphosphates. While there are phosphates of iron and aluminium the phosphate of lime is the only one that is used to any extent in the manufacture of "super." All phosphates are insoluble in water. They are not capable of feeding the plant directly—they must first decay; hence the use of a phosphate depends upon the rate of decay or time required to change to a state in which the phosphoric acid contents become "available" to the plant.

Phosphate rock is, in large part, made up of tricalcic phosphate, ($Ca_3 P_2O_8$) or ($3CaO, P_2 O_5$); the balance is made up of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), phosphate of iron ($Fe PO_4$), phosphate of aluminium ($Al PO_4$), calcium fluoride ($Ca F_2$), etc. Tricalcic phosphate is called bone phosphate because the substance is identical with that of which about 60 per cent. mammalian bones is composed, while the excrement of some also contains the same substance. The brachiopods lingula and orbicula, also conularia, serpulites, and some crustaceans, contain phosphoric anhydride. The valuable element in bones, mineral phosphates, &c., is the phosphorus. Phosphorus only occurs in nature in combination with other elements. Several combinations are known, but the three to be considered in this connection are—(1) Tricalcic phosphate (first mentioned, and formula given), (2) phosphoric anhydride (P_2O_5) and (3) orthophosphoric acid (H_3PO_4), which may also be written ($P_2O_5, 3H_2O$); this shows the phosphoric anhydride formula and water. In this form the phosphorus can be taken up and carried in solution in percolating rain waters. Guano deposits and beds of rock containing phosphoric acid exist, and have existed in past ages, some of which are of great geological age. Percolating rain waters, containing carbonic and other organic acids, leach or lixiviate such beds, and a

they filter through other limestone beds a chemical change takes place, and the phosphoric anhydride replaces the carbon dioxide. The change may be shown thus—

Phosphoric Acid.	Limestone.	Water.	Carbon Dioxide.	Rock Phosphate.

$$2H_3PO_4 + 3CaCO_3 = 3H_2O + 3CO_2 + Ca_3P_2O_8$$

The phosphoric acid contained in animal bone is, as already stated, in the form of phosphate of lime; hence the term "bone phosphate" has been applied to all phosphates that contain their phosphoric acid as phosphate of lime, notwithstanding the fact that the substance may be contained in either bone, rock, pebble, or mineral. In bones, bone phosphate has an organic origin; in minerals, it may have been derived from rock masses of partly or wholly organic origin, or be contained in rocks without any organic connection whatever, viz., in igneous or volcanic rocks, or in metalliferous veins. (The decomposition of the mineral apatite in pyritic veins and lodes might account for the phosphorus occuring in so many ironstone deposits.) In phosphate deposits the origin may be either the excreta of fish (coprolites) and the remains of fish themselves, or the shells of bivalves (phosphatic nodules may, in some instances, have originated in this way), or in the excreta of countless sea birds that fed on fish and the bodies of the birds themselves.

Protracted favorable conditions would doubtless produce a concentration of phosphoric anhydride; and it does not affect the commercial aspect whether the phosphorus was derived from guano beds resting directly on the limestone, that subsequently becomes enriched with phosphoric acid (as probably has been the case at Christmas, Ocean, and Sombrero Islands), or was brought from a distance; nor does the origin of the phosphoric acid. The succeeding notes on the several deposits by different authors on this question show that widely different opinions are held.

Each separate occurrence had its own peculiar origin, and one explanation will not fit all. It would, however, appear that to produce a suitable tricalcic phosphate the phosphoric acid must have access to a limestone bed, and if the "favorable conditions" exist long enough the whole bed will become phosphatised. It has been noted in many instances that phosphate rock occurs in hollows and pockets in limestone beds, and this is easily explainable by supposing that a concentration of phosphoric-acid-bearing waters had access to those places and phosphatised the limestone to greater depths in those places. I prefer this explanation to that of having to suppose that the hollows in the limestone existed before the phosphate rock was deposited in them; in other words, I prefer the chemical changing of the rock theory to the mechanical deposition in the majority of cases, though examples of both perhaps exist. Willard Hayes, in the United States Geological Reports, 1898-99, p. 633, states, that the brown phosphate rock of Tennessee is supposed to have been derived from the weathering of certain phosphatic layers, occurring at various horizons in the Lower Silurian limestone, which forms the basin of middle Tennessee.

In the Smithsonian Institution volume for 1899 it is stated that "apatite and phosphorite (1) may originate from segregation from surrounding rocks contemporaneously with their metamorphism and crystallisation (*e.g.*, gneisses); (2) from fumaroles, brought up in vapors along lines of contact with calcareous materials. Phosphates may be a secondary product from the leaching of rocks containing phosphoric acid. Carbonate of lime is more soluble than tricalcic phosphate; hence the common occurrence of the decalcification of pre-existing chalk and other limestone rock by percolating meteoric waters. When phosphates occur with oxide of iron the indications point to both having had an organic origin."

"Rock phosphates may have originated through the rapid alteration in temperature in the ocean brought about by ocean currents, or altered degrees of salinity, either of which might kill marine organisms in great numbers, and their remains might furnish the necessary phosphatic matter for phosphatic nodules. It seems that the cretaceous and tertiary deposits in various parts of the world may have formed under similar conditions."

Professor Cox ascribes the Florida phosphate deposits to the mineralisation of ancient guano, and he thinks the sand which forms the overburden, covering the almost entire peninsula of Florida, was blown over from the sea beaches.

The Tennessee rock phosphates, Hayes thinks, are due to the slow accumulation on sea bottoms of phosphatic organisms (lingulæ) from which the carbonate of lime was gradually removed by the leaching action of carbonated waters, leaving the less soluble phosphate behind. Teall thinks that in some cases the replacement may be effected through the agency of alkaline (principally ammonium) phosphate, which has leached down from overlying guano. Aluminus phosphates in caves may be formed through the action of ammonium phosphate arising from decomposing organic matter on clay of the floors of caves. Sea fowl excretions, when unleached, are relatively poor in phosphatic matter and rich in salts of ammonia; the more soluble constituents are leached out by rain waters, leaving the less soluble phosphates together with impurities in the shape of alumina, silica, and iron oxides.

Dana describes *guano* as a bone phosphate, mixed with the hydrous phosphates and generally with some calcium carbonate, and often a little magnesia, alumina, iron, silica, gypsum, and other impurities. It often contains 9 per cent. or 10 per cent. of water. It is often granular or oolitic; also compact through consolidation produced by infiltrating waters, in which case it is frequently lamellar in structure, and also occasionally stalagmitic and stalactitic. Its colors are usually greyish-white, yellowish and dark brown, and sometimes reddish, and the lustre of a surface of fracture earthy to resinous.

V.—MINERAL AND ROCK PHOSPHATE DEPOSITS.

1. *True Mineral Phosphates.*—Apatite (and its massive radiated variety, called "phosphorite") is the only true mineral from which phosphoric acid for fertilisers is obtained. When pure this mineral carries from

89 per cent. to 92 per cent. of bone phosphate. The apatite-bearing lodes of Canada are amongst the largest known; and the Norwegian are also important, where it has been mined for many years. At one time the Canadian apatite or phosphorite mines of Quebec and Ontario had an annual output of 25,000 tons; the highest grade contained 40 per cent. of phosphoric acid. On account of the Florida phosphate discoveries these workings are now practically abandoned. *The Spanish mineral phosphate mines*, which at one time produced considerable quantities of 50 per cent., 60 per cent., and 70 per cent. phosphates are no longer worked, apparently for the same reason. It occurs in rocks of various kinds and ages. Other occurrences are in Bohemia, Bavaria, United States, &c.

2. *The Amorphous Phosphates or Phosphate Deposits* are of far greater economic importance than the above. They are largely composed of bone phosphate. Not having any definite chemical composition, nor crystallographic or optical constants, they cannot be said to belong strictly to pure mineralogy. They are variously known as phosphatic nodules, coprolites, bone beds, phosphate beds, guano, phosphate rock, &c. *Phosphatic nodules* occur in many fossiliferous rocks of different ages, are irregular in form, and range from the size of a pea, or larger, up to a ton; the larger masses often being formed by the union of many small nodules. They have no crystalline structure, but sometimes are distinctly concretionary. In color they vary from light-grey to brown, and rarely jet black. Chemically, according to Dana, they usually consist of from 50 per cent. to 60 per cent or more of bone phosphate, with 6 per cent. to 8 per cent. of calcium carbonate, 4 per cent. to 5 per cent. of organic matter and moisture, and a variable amount of sand. They vary in hardness from 2 to 4, and in specific gravity from 2·2 to 2·5. The nodules are accompanied by the remains of marine life of various forms, sharks' teeth, &c. Phosphate deposits occur in many parts.

The South Carolina Rock Phosphates have been extensively mined since 1868. Phosphatic nodules are abundantly developed in tertiary strata there. According to Voorhees, these are found both on the land and in the beds of rivers in the vicinity of Charleston, and are sometimes called "Charleston phosphates." The deposits vary in thickness from 1ft. to 20ft. through, in which the phosphate is disseminated. The nodules range in weight from an ounce to over a ton. These nodules are irregular, non-crystalline masses, often full of holes, which contain clay or other non-phosphatic materials. That obtained from the river is called "river phosphate" or "river rock," and that from the land "land phosphate" or "land rock." The two varieties do not differ materially in the content of phosphoric acid. The rock contains from 26 per cent. to 28 per cent. of phosphoric acid. Its uniformity in connection with the fact that it contains but small percentages of compounds of iron and alumina—substances which prevent its best use by the manufacturer—make it a highly satisfactory source of phosphoric acid. The river rock is secured by dredging; that from the land is largely dug. In either case it is washed to remove the adhering matter, and then dried, when it is ready for grinding or shipment. When finely ground it is called "floats." It is sometimes

used upon the land simply in this form with satisfactory results. About 500,000 tons were raised in 1896. In 1886 the South Carolina phosphates were $5 and $6 per ton. The beds lie at an accessible depth; the easy approach, the abundance of water, fuel, and labor, and a climate that permits mining operations to be carried on throughout the whole year, combine to make them the cheapest. Three grades are sold, viz., 50 per cent. to 52 per cent., 55 per cent. to 56 per cent., and 58 per cent. to 60 per cent. of tricalcic phosphate. They are ground to go through a sieve of eighty wires to the inch.

A fair average of the chemical composition of the Charleston phosphates, according to Wyatt, is—Water and organic matter lost on ignition, 8·00 per cent.; phosphate of lime, 59·63 per cent.; carbonate of lime, 8·68 per cent.; iron and alumina (calculated as oxides), 6·60 per cent.; carbonate of magnesia, 0·73 per cent ; sulphuric acid and fluoride of lime, 4·80 per cent.; sand and siliceous matter, undetermined, 11·56 per cent.—total, 100·00 per cent.; and it is proved that these phosphates are admirably adapted for manufacturing chemical fertilisers. A speculative quantity of 750 tons to the acre would show this State to be equal to a yield of 14,000,000 tons, which estimate, Wyatt thinks, may be relied on; and he thinks that South Carolina and Florida are capable of yielding far more than the entire needs of the world far into the future.

Memminger states that the South Carolina phosphate beds, at the present rate of production, may last thirty-five years.

The Florida Rock Phosphate deposits were, according to the same authority, discovered in commercial quantities in 1888, since which time very great progress has been made in developing the deposits, which occur in a number of forms—First, "soft phosphate," a whitish product, somewhat resembling clay, and largely contaminated with it; second, "pebble phosphate," consisting of hard pebbles, occurring both in river beds and upon the land, and mixed with other materials; and third, rock or "boulder phosphate" which occurs in the form of stony masses or boulders, both large and small. These three forms also differ widely in composition, both in reference to their contents of phosphoric acid and in respect to other substances. The soft phosphate is the poorest in phosphoric acid. It is easily prepared and is largely used directly upon the land. It is also the most variable in composition, ranging from 18 per cent. to 30 per cent. The pebble rock is also variable in composition, though, when washed free of sand and clay, it is richer in phosphoric acid than the soft variety. Good samples contain as high as 40 per cent. and over of phosphoric acid. The bulk of the Florida phosphate is believed to exist in the pebble form. The rock or boulder phosphate, though apparently much less in amount, is more uniform in composition, and is much richer than either of the other forms. The clean, dry, boulder phosphate often contains as high as 40 per cent. of phosphoric acid, far exceeding in richness the South Carolina rock phosphate. Dana says the beds have been traced along a line nearly 250 miles long, running a little east of south into Charlotte Harbor. The main point of interest is at a place called Dunnellon. The Florida phosphate discovery entirely revolutionised the phosphate market.

From the Smithsonian volume above referred to the following has been extracted anent this splendid deposit:—(1) The original hard rock phosphates lie in regular beds *in situ* as well as in boulders a few feet below the surface of superficial sand. The beds are usually 4ft. to 5ft. thick, and the rock carries from 30 per cent. to 35 per cent. of phosphoric acid. In other places the phosphate occurs in nodules in the beds, which is not so high in phosphoric acid. The original beds occur in rocks of Miocene age, and, with the exception of the soft phosphates (which arises from the decomposition of the hard varieties and only average 20 per cent. to 25 per cent. of phosphoric acid), they underlie distinct regions, each class being separate or but slightly commingling with one another. The hard rock is a hard, massive, close-textured, homogeneous, light-grey rock showing large and small irregular cavities, which are usually lined with secondary mammillary incrustations of tricalcic phosphate, the general appearance somewhat resembling calcareous deposits from hot springs. Whether the whole rock phosphate proper was derived from the decomposition of the nodular form is not made clear, but much of it owes its origin to that. Phosphatic solutions have penetrated both Miocene and Eocene strata, thus giving rise to hard rock phosphates carrying 36·65 per cent. of phosphoric acid. In the Miocene it lies in phosphatic sands, clays, and other material. In the Eocene it occurs in boulder deposits in a soft material: the deposits underlie sands of from 10ft. to 20ft. in thickness, and have been penetrated to a depth of 60ft. The phosphate deposit in this case is white, the boulders of rounded and irregular outline varying from 2ft. to 10ft. in diameter, and are all of secondary origin. None of the hard rock deposits of the Eocene originated in the positions they now occupy. Numerous varieties and variations from the above description of the hard rock occur. Mr. Eldridge's is considered one of the principal reports on the Florida deposits. A bibliography accompanies the article.

On the discovery of phosphates in Florida land went up from $1·50 to $150 and $200 per acre. Wyatt states that the hard rock beds are estimated to extend for 160 miles long by twelve miles wide. The pebble beds spread out to thirty miles wide. The landscape is an extended, monotonous, though often timbered, prairie. The phosphate beds have been subjected to some erosion, both at and beneath the surface; the latter is surmised from the numerous sink holes occurring through the removal of the underlying limestone. In Western Florida the upper formation is Miocene, of thin-bedded horizontal limestones. This area has few sink holes. In the hard rock areas the general elevation is less than 75ft. above sea level. Wyatt thinks that chemical solution has exceeded mechanical abrasion in producing the present river channels and moulding the general topographical features. Pines grow in the sandy areas, and deciduous growths predominate in the hummock lands. In the lowlands cypresses, oak, gum, ash, magnolia, and bay are the chief timbers. In explanation of certain phenomena, Wyatt remarks that limestone acted upon by carbonic acid waters would be removed, while the greater part of the less soluble phosphate rock would remain behind, or be washed into caves and hollows and redeposited there, the

limestone walls of which would be subsequently leached away. Phosphate of lime is soluble in waters saturated with carbonic acid gas. The addition of chloride of sodium increases the solubility. Loss of the quantity of carbonic acid gas would mean the precipitation and redeposition of the phosphate rock. The redeposition of $Ca_3P_2O_8$ in cavities would give it the boulder appearance. The redeposition in cracks and amongst shells and drifts would account for its present mode of occurrence. These, by being on the surface, could be rolled into boulders and form, with other material, agglomerations of phosphate rock, finely-divided *débris* or soft phosphate, sands, clays, and marls, all jumbled up together, making a heterogeneous mass, in which would be flint rock cemented together with soft phosphate or clay. He also thinks that the land and river pebble of South Florida originated in an exactly similar manner to the hard rock phosphates, with the difference that the phosphate of lime, which was suspended or dissolved in the mud or silt, was deposited on a surface of limestone and underwent a subsequent process of segregation and nodular concretion. Hard rock sometimes extends over several acres uninterruptedly, being combinations of the original pocket, and the mound formation, with overlying sand without phosphate 8ft. to 10ft. thick on an average. The underlying rock is sometimes an aggregation of enormous boulders intermixed with boulders of flint and limestone, all cemented together with thin layers of clay, and sometimes in the form of small fragments of phosphate boulders embedded in a white plastic or friable mass resembling kaolin. The white material is known as soft phosphate, and is, like the fragmentary rock, doubtless the result of a natural disintegration of the hard boulders by rolling, attrition, or concussion. The thickness of such beds varies from 5ft. to 50ft. before reaching the limestone bottom. These "pockety and mound" formations frequently terminate very abruptly, and graduate into a fragmentary material that shows on the surface. When pockets are of considerable depth they yield large quantities of merchantable phosphate, but they are frequently very superficial and so intermixed with other material as to be unprofitable. The open-cut system is found to be the best to work these deposits on. Wyatt estimated the yield from a typical area as follows:—5,120 acres of land yielding, say, 5,000 tons per acre, equals 415,000 tons. of which 55,000 tons might be high grade, say, 80 per cent., and 125,000 tons of *débris* and seconds containing from 60 per cent. to 65 per cent. The washing process is made use of to remove the iron and alumina that adheres to the rock in the form of clay. The freight by rail of Florida hard rock to Fernandina, the port of shipment, is about $2·25 per long ton. Those that can send it to Port Tampa pay $1·50 per ton, but this is not much cheaper, that being a bad port. The pebble beds are not so erratic in habit as the boulder beds. The pebble phosphate stratum varies in thickness from a few inches to 30ft. with an overburden of sand and clay of about 8ft. average. Peace River lands are the most important for pebble. The pebbles vary in size from a grain of rice to about 1in. in diameter, and are intimately mixed up with the bones and teeth of numerous extinct species of animals, birds, and fish. The cost of raising, drying, screening, and loading

river pebble on the cars is about $1·75 per ton, which is said to be the lowest in the history of the world's phosphate mining. Prior to 1894 the State proposed to institute a royalty of 50c. on all rock up to 55 per cent. from rivers, 75c. on 55 per cent. to 60 per cent., and $1 for over 60 per cent.; and tributers had to start operations on the prescribed area within six months from signing the agreement. A plant that will bring up 40 tons to 50 tons per day costs about $84 per day to work. Freight from the pebble region does not exceed $1·25 per ton. The hard rock and boulder phosphate is white, blue, yellow, or brown; it varies much in quality and in the percentage of iron and alumina it carries. Wyatt made the values as follows :—

	$Ca_3P_2O_8$	Iron and Alumina.	Silica and Silicates.	Carbonic Acid.
120 samples of boulders gave	80·49	2·25	4·20	2·20
237 " boulders and *débris*	74·90	4·19	9·25	1·90
148 " soft white phosphate	65·15	6·20	5·47	4·27
84 " pebble from Peace River ..	61·75	2·90	14 20	3·60
92 " pebble from drift beds, Polk country	67·25	3·00	10·40	1·70

Florida yielded 3,000 tons of phosphates in 1888; in 1889, 4,500 tons; in 1890, 45,500; in 1891, 112,500; in 1892, 300,000; and for 1893 an equal quantity was estimated. In 1890 about 600,000 tons of rock from all sources were sold in United States of America, and of this quantity South Carolina produced 537,000 tons and Florida 46,500 tons. The average value was $7 for rock containing 60 per cent., and $12 for 75 per cent. to 80 per cent. rock f.o.b.. During 1892 700,000 tons were sold, of which South Carolina supplied 350,000 and Florida a little over 300,000 tons. The prices fell in this year to $4·50 and $6·50 for the same respective qualities.

C. G. Memminger, in an article in *The Mineral Industry*, 1891, states that the Florida rock phosphates occur north and south for 240 miles by thirty miles wide. The deposits occur only at widely-scattered points, and those of commercial value form but a very small percentage of the total phosphate-bearing area. In 1899 444,675 tons and in 1900 343,120 tons of hard rock were produced. This (hard rock) area is ninety miles north and south by eight to ten in width. The deposits are simple pockets yielding from a few tons to many thousand. The boulders vary in weight from a few pounds to many tons. The rock is washed and dried. Removable washers are now used, so that when a pocket is worked out it can readily be shifted to a new site. A convenient-sized washer has a capacity of 40 tons to 50 tons of clean rock in twenty-four hours; the material put through averaging 12 per cent. to 15 per cent. phosphate, and the rest being rubbish. The whole of the material is crushed and washed to remove the clay, then picked over and dried in kilns. The average cost of production, ready for shipment

at the mines, is from $3·50 to $4 per ton. The best grade product is limited in quantity. In 1901 230,886 tons of land pebble were mined. The pebble occurs roughly rounded, and of greyish or brownish color, varying in size up to 2in. in diameter. The beds vary from a few inches to 18ft. in thickness, averaging 10ft. for the district. The pebble usually represents less than 25 per cent. of the mass. An interesting account of the process by which this rock is recovered is given in the above work, p. 515. The present cost of production f.o.b. at the mines is from $1·50 to $2 per ton—a figure that will doubtless increase materially in the near future. At the present rate of production the deposits, containing 68 per cent. and upwards of bone phosphate and low in iron and aluminium oxides, will be exhausted within a few years. Those containing 64 per cent. to 67 per cent. bone phosphate and 4 per cent. to 6 per cent. iron and aluminium oxides are in very large reserves. Fifty-four thousand five hundred and six tons of river pebble were produced in 1900.

The Tennessee Rock Phosphate Deposits were discovered in November, 1894, since which time they have been exploited, and a rapid development made. This phosphate differs from the phosphate of South Carolina and Florida, says Voorhees, in that it does not exist as nodules, pebbles, or boulders, but in veins and pockets, and therefore does not need to be washed and dried previous to treatment. While the phosphates from the various deposits are not uniform in their composition, it is possible to secure large quantities that exceed 30 per cent. to 32 per cent. of phosphoric acid, or 70 per cent. or over of bone phosphate, and that are relatively free from deleterious substances, thus making them not only a rich, but a valuable source of supply for the manufacture of superphosphates. Memminger divides, according to its color, the Tennessee phosphate into blue, brown, and white rock; and the area of the beds is approximately ten miles by twelve miles. The blue phosphate rock occurs in horizontal beds lying on and conforming to the country limestone. Above it is a black Devonian shale. The average thickness of the workable deposits is 18in. The great bulk of the rock has to be mined under cover. The high cost of mining is largely set off by the reduced cost of preparation, cleansing being unessential. This is the only phosphate deposit as yet found in the United States that can be mined and shipped without treatment. The average bone phosphate percentage in this rock is 70 per cent. and 2·5 per cent. to 3 per cent. iron and alumina. The blue rock deposit is large. The brown rock area is three miles by eight miles, but not in a continuous bed, which, however, conforms to the irregularities of the underlying limestone, and is 36in. average thickness. The overburden consists of loamy soil and is of varying thickness. The average yield per acre is 4,000 tons. Two grades are guaranteed—(1) 78 per cent. bone phosphate, and 4 per cent. iron and alumina; (2) 75 per cent. bone phosphate, and 5 per cent. iron and alumina. The white rock occurs near Tennessee River; it resembles Florida land rock in appearance and occurs with chert in pockets of variable size. No other large deposit of this class has so far been developed. It is high-grade rock.

Belgian Phosphates.— Belgium has great advantages in this field over most of the European countries, owing to its favorable situation as regards transportation, cheap fuel and labor, and especially the low cost of sulphuric acid, which is recovered as a by-product at the zinc smelters. It is stated in *The Mineral Industry* that 60° acid is delivered at the works at a cost of from 1·60fr. to 1·75fr. per 100 kilogrammes, or $2·80 to $3·07 per short ton. Aikmann says that the rock is found in layers and in pockets, and that it varies in bone phosphate contents between 25 per cent. and 65 per cent. On the whole it is of poor quality and unsuitable for the making of superphosphates. One hundred and forty-five thousand tons were raised in 1886. The beds occur in cretaceous chalk. (Parke.) There are phosphate beds in rocks of the same age and character in the south of England.

France.—The so-called Somme phosphate beds occur in cretaceous chalk in the north of France. It is of higher quality than the Belgian, and contains from 50 per cent. to 80 per cent bone phosphate. Up to 1888 150,000 tons, Aikmann states, had been raised, of which about one-half contained from 70 per cent. to upwards of 75 per cent. There are four grades in the market, viz., 50 per cent. to 60 per cent., 60 per cent. to 65 per cent., 70 per cent. to 75 per cent., and 75 per cent. to 80 per cent. The highest quality furnishes the chief material for the manufacture of high-grade superphosphates. In *The Mineral Industry* it is stated that the production of phosphate rock, which amounted to 645,868 metric tons in 1899, is exceeded only by that of the United States. The most productive fields are located in the departments of Somme, Pas-de-Calais, Aisne, Oise, and Meuse, the department of Somme alone producing 300,000 tons. Deposits are known to occur in the Pyrenees Mountains, and will probably be exploited in the near future. Specimens from this region, according to David Levat, show 60 per cent. to 70 per cent. tribasic calcium phosphate. Among the European countries France is the largest manufacturer of superphosphate, and also the largest consumer. In 1899 the total output was about 950,000 metric tons, and the consumption 980,000 tons; the consumption in Germany amounting to about 825,000 metric tons, a small portion being imported. The crude material is derived mostly from the United States and Algeria.

At Boulogne, &c., in the north of France, the phosphate rock—as coprolite beds—occurs in chalk, the coprolites being dark-grey nodules. In the east of France phosphate of lime is obtained from the Greensand, and that from the departments of Lot and Lot-et-Garonne from calcareous soil. This latter, according to Lock, occurs in pockets in fissures in the limestone, and also in thin layers near the surface. These are covered with an alluvial soil and clay containing phosphates, but much contaminated with iron and other impurities. The pockets, of all shapes and sizes, and sometimes reaching 100ft. deep, are generally traced and indicated by narrow vertical veins of deposit, which rise from them to the surface, and are mostly found in the highest ground. It varies greatly in appearance, texture, and composition. Occasionally it is found in snow-white compact masses, breaking with an earthy fracture, and of moderate degree of hardness. The more ordinary kinds are a

dark-yellow or brown, dense and hard; but it is frequently found of a dark-agate color, somewhat resembling the inside of broken flints, of a waxy lustre, stratified and intersected with thin layers of iron oxide. The white specimens are generally the richest, some being as high as 85 per cent., with a minimum ($\frac{1}{2}$ per cent.) of iron, &c.; but the bulk only contain 70 per cent. to 72 per cent. of tricalcic phosphate, and with 4 per cent. or 5 per cent. of iron, &c. The surface phosphatic earth finds ready sale on the spot. The best varieties of these phosphates are well adapted for the manufacture of superphosphate.

Algerian Phosphate Deposits.—The phosphate deposits in Northern Africa are making their influence felt on the market. All the mines in Algeria have railway connection with the seacoast, and, owing to their favorable situation and high quality of the product, are strong competitors of American rock in European markets. The shipments from Bone, Algeria, in 1900 were 232,353 metric tons, against 246,406 in 1899. Some cargoes to England carry 60 per cent. to 70 per cent. of bone phosphate. Parke, speaking of Tunis and Algeria (quoting from "Memoirs of the French Society of Civil Engineers," August, 1897), states—The beds are of Eocene age, the phosphates occurring in nodules in marl or as phosphatic limestone. M. Chateau, a French mining engineer, estimated the Algerian beds to contain from 150,000,000 tons to 300,000,000 tons of phosphate rock.

Tunis Phosphate Deposits.—The production from the deposits at Gasfa in 1899 was 70,000 metric tons; in 1900 83,000 tons during the first six months. A new field is about to be opened on the plateau of Kalaa-es-Senam, near the Algerian frontier, the right of exploration having been sold in December, 1900. The deposits range in thickness from 12 metres to 15 metres, of which about 2 metres is high-grade rock. An average analysis shows 60 per cent. calcium phosphate, 25 per cent. calcium carbonate, 0·25 per cent. iron oxide, and 0·50 per cent. alumina. The distance from the nearest mines to Tunis, the nearest port, is about 250 kilometres, and the two points are to be connected by a prolongation of the railway from Tunis to Pont de Fahs. The beds are of Eocene age. (Parke.)

Egyptian Phosphate Beds.—According to the report of the German Consul at Cairo extensive deposits have been found in the desert east of Kenah, near the caravan route leading to Kosseir, on the Red Sea, and also in the Dakleh Oasis of the Lybian Desert. The rock is said to be exposed in many places, and can be worked without much difficulty. Analytical tests show the presence of phosphoric acid in amounts corresponding to 40 per cent. to 60 per cent. calcium phosphate, which is too low to permit of the material being exported, although it may be of domestic importance.

Caribbean Phosphates, on Monks Island, run from 60 per cent. to 80 per cent. of bone phosphate.

There are other guano and rock phosphate deposits, *e.g.*, on the islands of Navassa, Curacoa, and Maldon. The latter is situated in the Pacific Ocean, and is said to yield a granular phosphate high in phosphoric acid. The Arbrohlos Islands, off the west coast of Western Australia, are reported to contain phosphate rock.

Cambridge Phosphate Deposit.—The Upper Greensand beds in Cambridgeshire, England, yield small nodular hard masses of a grey color (supposed to be coprolites), or occasionally concretions around bones. Fish teeth and vertebræ occur with these. Their average composition (as given by Lock) is 55 per cent. to 60 per cent. tricalcic phosphate, 12 per cent. to 18 per cent. calcium carbonate, 3 per cent. to 5 per cent. alumina and iron (but sometimes as high as 10 per cent. and 14 per cent.), 2 per cent. to 4 per cent. calcium fluoride, and insoluble matter 6 per cent. to 8 per cent. The coprolite-bearing stratum is not more than 1ft. thick, and the average yield 300 tons per acre. There appears to be difficulty in making more than a 25 per cent. soluble phosphate from the rock.

In *Suffolk and Bedfordshire* also coprolitic beds occur as well.

In *Montgomeryshire, Wales, there are Phosphatic Deposits.* The rock as mined carries much worthless matter, and to dress it up to 46 per cent. standard costs 3s. per ton. Its color seems to be prejudicial to its sale, as the industry is languishing. (Lock.)

In *Russia Coprolite Beds* occur, but they are of poor quality.

The Christmas Island Phosphate discovery was described by C. W. Andrews in the *Geographical Journal* of January, 1899, and in a monograph, from which the following information is taken. Christmas Island is one of the most interesting of the lonely islets in the Indian Ocean. It lies about 190 miles south of Java. It is the summit of a submarine mountain, more than 15,000ft. high. The seas around are of enormous depth, and soundings of 1,000 fathoms occur within two or three miles of its coasts. To the north and north-west is Maclear Deep, in which 3,200 fathoms were found, and to the south is the more extensive Wharton Deep, with upwards of 3,000 fathoms. Seen from the south-west the island appears as a long green ridge, nearly level at the top, there being only slight elevations at the north-west and south-east ends. The ridge descends seawards in a succession of terraces. A submarine terrace, in the shape of a fringing reef, is being formed round the greater part of the island. Outside the edge of this reef the water deepens suddenly. The island contains about forty-three square miles, is twelve miles long, and varies in width from three and a half to nine miles, and consists of a central plateau. The terraces are separated by slopes or cliffs. From the edge of the plateau there is (1) a steep slope strewn with blocks, (2) a broad terrace followed by a similar slope, (3) a second terrace terminating in a cliff 200ft. or 300ft. high, (4) a shore terrace sloping gently down to the sea cliff, (5) the present fringing reef. The average height of the plateau is about 800ft. Along the raised rim of the plateau there are a number of hills; the highest (Murray Hill) is 1,170ft. The summit is formed of dolomitic limestone. Shelly limestone beds and beds of volcanic ejectamenta occur lower down. The dolomitic limestone shows traces of gasteropod shells. Over North-East Point is another elevation (Phosphate Hill), which, though not so high (900ft.), is particularly interesting on account of the extensive deposit of phosphate of lime which is found there. This substance is strewn over

the surface in blocks of all sizes, and in some places it is found to a considerable depth; in others, however, it can be seen to rest directly on an irregular surface of dolomitic limestone, occasionally pinnacles of which project through it. At the northern edge of the hill the phosphate is found on both outer and inner slopes, but further south on the plateau side only, the outer being occupied by a reef of limestone, which descends to the terrace beneath in a low cliff. The area actually covered by this thick deposit of phosphate of lime is about half a mile long by a quarter of a mile broad, but an immense quantity occurs in the form of irregular nodules and blocks scattered over all the slopes and terraces of this part of the island. There are other less extensive deposit beds over Flying Fish Cove, and also at several points along the eastern edge of the plateau. Probably, when the islands were still low, and not covered with forest, as they are now, they formed the homes of myriads of sea birds, and the guano thus formed, after undergoing alteration mainly through loss of its organic matter, gave rise to the hard phosphatic rock now existing. At the same time the limestones on which it rests have often been phosphatised, and lumps of coral, consisting mainly of phosphate of lime, are sometimes found. The extensive accumulations of guano which must have taken place point to a time when the rainfall was much less than at the present day—a condition which may, at least in part, have been dependent on the circumstances that the islands were low and probably free from forest. The phosphate rock is hard, brownish-white, and of other darker tints, and has a waxy lustre. The phosphate has replaced the carbonate of lime in a limestone of organic origin, which latter is largely built up of the remains of foraminifera, the forms of which may be made out when the rock is sectioned and examined microscopically. Bone fragments have also been detected in the phosphate rock. Sometimes the phosphate rock has a banded, semi-transparent, agate-like structure, in concentric layers, apparently deposited from solution. The average composition of the phosphate is 39 per cent. phosphoric acid, 51·5 per cent. lime, 3·5 per cent. carbonic acid, 2 per cent. iron and alumina, 4 per cent. being made up of magnesia, water, fluorine, and other substances; with only ·2 per cent. silica. The island appears to have remained uninhabited until the last thirteen years. When Mr. Andrews left it, viz., in May, 1898, the total population was about forty souls, of which a number of coolies had recently been imported from Java to make the necessary preparations for working the valuable deposits of phosphate of lime. The exported rock from Christmas Island is stated to contain 80 per cent. of bone phosphate. The discovery is one of the most recent as well as intrinsically important to Australia, and extensive shipments are now made periodically to Australia and Japan.

On Ocean Island, in the Gilbert Archipelago, which lies east of New Guinea, a still later discovery of rock phosphate was made. No literature is available on the subject, but the occurrence is reported to resemble that on Christmas Island, and that beautiful examples of phosphatised coral are found there. Some samples show a mammillated, oolitic, and

concretionary structure, and the color ranges from brown, and also purplish-brown, to white. Both hard and soft rock are imported to Australia. The grade is not quite so high as that from Christmas Island.

Thomas Phosphate Powder is a waste product from the manufacture of steel from phosphatic iron ores. It is produced in large quantities in England, France, and Germany. It contains from 15 per cent. to 20 per cent. of phosphoric acid in the form of phosphate of lime in connection with large amounts of lime and oxide of iron. It is used almost altogether in the form of a fine powder, since it is not suitable for the purposes of the manufacturer. It is stated that the best results from Thomas phosphate are obtained when applied to sandy, loamy, moderately moist soils, and that but little benefit is noticeable in clay and black soils. In 1896 Europe produced 1,525,000 short tons of basic slag (Thomas phosphate is the phosphatic basic slag produced by the Thomas steel process) equivalent to 800,000 tons of high-grade phosphate rock, of which Germany consumed 800,000 tons.

Meat Meal Guano contains 4 per cent. to 8 per cent. of nitrogen and 13 per cent. to 20 per cent. phosphoric acid.

Fish Guano contains 8 per cent. to 10 per cent. of nitrogen and 4 per cent. to 15 per cent. phosphoric acid.

Bat Guano contains 9 per cent. of nitrogen and 25 per cent. phosphoric acid.

At *Sombrero* the waters which have filtrated through the guano have altered the coral rock adjoining, turning it more or less completely into phosphate of lime, of a yellowish or brownish color; and phosphatic stalagmites and stalactites, resinous in fracture, are common. The phosphate rock, according to a recent account by J. W. Spencer, occurs in pockets in, and reposes on, Pliocene limestone, showing—when the phosphate is removed—handsome colonies of coral. The supplies are said to be pretty well exhausted. Sombrero is a small island in the Antillean Archipelago, West Indies.

Redonda is another small island in the same group of islands, with a phosphate deposit on it, which is said to contain high percentages of iron and alumina.

The Clarendon (New Zealand) Phosphate Deposit.—Professor James Parke recently described a phosphate deposit that occurs in the Otago district, at a point about a mile west of Clarendon railway station, on an estate known as the Horseshoe. The discovery was made in 1891 by Mr. Ralph A. Ewing. The phosphate rock has been found in several places over the estate, which has an area of some two square miles, including, among other points of interest, the well-known lime quarries of Milburn. The neighborhood is open agricultural land, much of which is at present under cultivation. I extract the following information from the report:—Horizontally-disposed mica schist is the foundation rock over the area. This is overlain in all but a few places with more recent formations. First, and resting directly on the schist, are quartz grits and conglomerates (these, by the way, usually form the lowest member of the coal measures in Southern Otago). Glauconitic greensands, limestones (often glauconitic), and a soft brown sandstone follow

on in this order of succession, and the whole is covered in places by a flow of basaltic rock. The series of beds associated with the limestone lie nearly horizontal. The phosphate rock occurs in pockets in the limestone, and is covered in most places with an overburden of brown-colored sands. The age of the basalt flow, which covers all the higher hills, is post-Miocene; the brown sandstone is Upper Eocene; the limestone—divided into upper and lower—the glauconitic sandstone, quartz grits, and conglomerates are Eocene; and the mica schist is Silurian. The grits carry gold, but not in payable quantity. The coarse grade of the sandstone, and also the fossils found in it, are characteristic of shallow sea deposits; and the glauconite demands an absence of strong sea currents and a coastline free from the encroachments of fluviatile deposits. The Eocene strata were deposited, consolidated, elevated, and denuded prior to the eruption of the basalt.

The phosphate rock was first found at Discovery Point, where it rests on the upper surface of the limestone. Here it forms a massive outcrop from 12ft. to 18ft. high, and from four chains to five chains long. It consists of a very dense grey or yellowish-grey phosphate rock, very rich in calcium phosphate. In places it is nearly pure phosphorite, occurring in narrow-banded pale yellow and grey concretionary masses, possessing a tendency to exfoliate in layers when struck with the hammer. Cavities in this rock were found to be incrusted with a mammillary structure. The extent of the deposit at this place has not yet been determined.

Another outcrop of phosphate rock crops out on the side of the valley opposite Discovery Point, and near it several large masses of this mineral occur in a small depression in the hill, about 20ft. above this outcrop. These masses are obviously not *in situ*, and appear to have fallen from a higher elevation, which would tend to indicate two horizons of phosphate rock between the limestone and basalt.

At Kiln Point a considerable amount of stripping and trenching has been effected, and here much interesting information was obtained concerning the mode of occurrence of the phosphate rock. At this place the outcrop has been stripped for a distance of nearly two chains, exposing a very clear vertical section of the phosphate and underlying limestone. The phosphate varies from 3ft. to 12ft. in thickness, and rests in a series of pockets in the limestone. In the face behind the old limekiln there are three shallow pockets, the most southerly being 45ft. wide, the second 18ft., and the third about 22ft., varying in depth from 2ft. to 6ft. The pockets are separated from each other by ridges of limestone averaging 3ft. or 4ft. wide. The phosphate fills the pockets and rises above the level of the dividing ridge of limestone a height varying from 10ft. to 3ft., the greatest depth occurring at the north-east end of the section. The phosphate rock exposed in the face of the open cutting is much broken and crushed, and sometimes shows slicken-sided surfaces. It is yellowish-brown in color, with irregular seams and patches of whitish grey. The presence of sand renders it soft and friable, and of lower grade than that exposed at Discovery Point. At the most easterly point of the open cut masses of fairly pure phosphate rock contain inclusions of basalt, occurring in small angular

or nodular fragments, which are seldom over 4in. in diameter. In a deep narrow trench above the open cutting the phosphate is mixed with glauconitic greensands, which are said to be highly phosphatic.

The phosphate rock has been exposed by a long trench some twelve chains north of Kiln Point, but no feature of special interest is disclosed in this direction.

On the right side of the present quarry face the upper horizon of limestone has been eroded down to the lower, more sandy, and glauconitic horizon, on the irregular surface of which there rest two small patches of phosphate rock.

On the right bank of a small stream, near Sutherland's limestone quarry, there is a high face of phosphate rock resting in a basin in the lower horizon of limestone; and a few hundred yards south-west of Milburn quarry there is a similar but smaller outcrop, which also appears to lie on the higher part of the lower horizon.

The surface contours and the presence of basalt fragments in the phosphate rock at Kiln Point tend to indicate that the formation of the deposit took place in comparatively recent times, probably in the post-Pliocene period, and obviously since the present contours were determined; hence the phosphate deposit will be marginal, and follow the line of limestone outcrop, contouring around the slopes of the hills bounding the valleys and shallow basins.

The pockety mode of occurrence and the geological conditions of the Clarendon deposit bears some similarity to that of Western Florida. The evidence available from a surface examination shows that a large quantity of phosphate rock exists in the district, but until the deposits have been fully developed it would be obviously impossible to express the tonnage numerically. The purer phosphorite (at Milburn quarry) is often very compact, fine-grained, and hard, possessing also the banded, wavy, and chalcedonic structure of chert, or flinty quartz deposited from thermal waters, for which it was mistaken in the past at Milburn.

The Clinton (South Australian) Phosphate deposit was discovered in either 1899 or 1900, by a Mr. Barton, on the estate of the late William Fowler, and lies about three miles N.N.W., of the port of Clinton, on Yorke's Peninsula. Going in a north-westerly direction from Clinton, one passes over Pleistocene or recent alluvial land, under cultivation, that steadily rises some 200ft. in three miles. At this horizon patches of red and white chalcedonic rock occurs in patches, with casts of recent or Miocene marine shells through it, showing that the land has recently risen, and that the sea washed the foot hills of the Hummocks Range in this neighborhood within comparatively recent geological time. The range has its southern termination in a low range of hills hereabouts, that run in a north-south direction, gradually diminishing in height to the south. Their total elevation here would probably not exceed 400ft. above sea level. The highest portion forms a ridge that faces the east, and the ridge forms the watershed of several short dry creeks that take their rise on the crest, then run for a short distance over, and across the strike of the Cambrian rocks (of which the range is principally composed),

when they reach the alluvial plains that extend to the shore of Gulf St. Vincent. From the crest of the ridge to the sea-shell beds would vary in different places from half to one mile. Beneath the crest of the ridge eastward, and running parallel to it in a N.N.E. and S.S.W. direction, the rock phosphate formation occurs. It extends for over 104 chains and varies in width between eight and twenty chains throughout that distance. The general strike of the Cambrian rocks over the area occupied by phosphate formation is about N. 30° E.. and the dip is easterly 30° from the horizon at one spot where measured. The uniformity in strike and dip that prevails within the area overlain by the southern two-thirds of the phosphate formation—which, by the way, rides hard and unconformably on the Cambrian rocks—is to some extent broken by faults, jointing, and bending of the strata in different directions, and disturbances generally, in the northern portion, whereby along certain lines these rocks were brecciated and masses of rock were thrown down. This is evident from some of the exposures in the quarries. No very great displacement of the Cambrians was observed; the greatest being at the northern end, in the vicinity of the principal workings. No evidence was observed to show that the disturbances postceded the formation of the rock phosphate deposit, and the disturbances may date back to the time when the Cambrians were upheaved.

It is evident that during the time the phosphate deposit was forming the Cambrians were much eroded, and the configuration of the area over which it extends was much the same as it is to-day. The bays and hollows and gullies that run back into the ridge and that are now drained by the small creeks were in existence then; the physical features have been modified to some extent as erosion has proceeded.

A layer of alluvium, intermixed with concretionary and nodular lumps of travertine limestone, derived from the decomposition of rocks standing at higher levels, has spread itself over portions of the phosphate formation, in places partially, at others wholly, covering it; but in no case is this overburden likely to be of any great thickness over the area under notice, and, being of a loose nature, it can readily be removed. This overburden may have entirely covered the deposit at one time, but it now occupies only the ridges that separate the creeks from one another; the rest has been entirely removed and carried down to lower levels through the creek channels, thereby exposing the edges of the deposit. Not only has the overburden been removed, but in Baker's Gully and the next gully to the south these two creeks have cut their way right through the phosphate formation (that is, if it ever existed there), but also for a few feet into the underlying Cambrians. On the northern end the same thing has to some extent take place, but in that quarter it is questionable, for other reasons, whether the phosphate formation ever had any quantity of real foreign overburden.

As already stated—and it is a point that should be noted—the phosphate formation rests directly on the Cambrian rocks, but it is possible, and also probable, that during the deposition of the phosphoric acid portions of the area were covered with alluvium. This would appear to

have been the case in the central gullies, where some old ironstone quarries are situated. A close examination of the rude stratification of the formation shows that it conforms to the physical features of the Cambrian rocks, for in whichever way the surface of the Cambrians undulate so the layers of the phosphate formation follow. These remarks are not intended to imply that an actual layer of phosphoric acid carrying material was actually laid down, but that some substance containing phosphoric acid in a soluble form was from time to time spread over the land. The phosphoric acid could have been derived originally from fish which were eaten by sea birds. The excrement from the birds, as also their decomposing bodies when they died on the spot, would supply phosphoric acid in a water-soluble form. No fossils have yet been detected in the formation, and for this reason its origin and geological age is uncertain, but the sheltered position which the deposit occupies and the way it occurs, viz., by spreading itself as a sheet over the slanting ground and up the sides of the hollows and hills to their very summits and around the rocky eminences, is just the place that sea birds would congregate together in. Pelicans, penguins, and sea gulls are known to congregate together in great numbers and make their home and nesting place in certain definite spots. It may be that the land stood lower at that time and that this spot was then right on the coast and favorably situated for a resting and nesting place. There is nothing known to me to lead one to suppose that a more or less continuous rock formation, such as would necessarily be implied in assuming the deposit to have had a coprolitic and fish-remains origin, or derived from the decomposition of phosphatic nodule beds, or had its origin in phosphatic material derived from phosphoric-acid-bearing outcrops of older rock (such as is the explanation given of the Tennessee deposit), or beds with lingula, orbicula, conularia, or serpulites. None of these latter explanations seem to fit the case.

There are bands in the Cambrian limestone full of nodular concretions, and it occurred to me that these might have afforded the phosphoric acid, but the samples tried yielded no trace. While admitting that the suggested guano-deposit origin is not proven, this suggestion would seem to meet the case better than any other.

Admitting, for argument's sake, that a guano deposit or a roosting ground for sea birds did exist over the area occupied by the phosphate formation, and that the phosphoric acid was derived from this source, then percolating rain waters, containing carbonic and other organic acids, would leach or lixiviate them, and as the waters filtered through to lower beds of rock, composed in large part of carbonate of lime, the phosphoric anhydride would replace the carbon dioxide, and rock phosphate would be formed (tricalcic phosphate).

$$2H_3PO_4 + 3CaCO_3 = 3H_2O + 3CO_2 + Ca_3P_2O_8$$

The fact has already been mentioned that blocks of rock phosphate have been turned up by the plough, but there are no outcropping edges,

such as one might be led to expect if the deposit was horizontally disposed, nor do large blocks show anywhere on the surface, such as would be the case if a horizontally-disposed young limestone rock formation had been phosphatised *(e.g.*, Christmas Island). The conditions here are different.

The western watershed of the creeks that run across the phosphate formation is composed of brown, yellow, and white dolomitic Cambrian limestones, which have weathered more slowly than the other members of this series, and now form the north-south ridge first referred to. These are superseded by fine-grained felspathic, calcareous, argillaceous, and quartzose sandstone bands of rock on the east, which are intercalated with limestone bands. The gritty bands are more permeable, and weather faster, as also do certain of the limestone bands, than do the dolomitic limestones. On the eastern side of and also running under the phosphate deposit is a dense dark-colored magnesian limestone, that breaks with semi-conchoidal fracture, and weathers very slowly; consequently it is seen to protrude through the phosphate deposit in several places. There are also bands of a dark-brown limestone rock, which occur in close conjunction with that last-mentioned, but also away from it, and the bands recur again and again, and together with the gritty and earthy limestone bands form the greater portion of the bedrock of the deposit. This limestone has distinctive features, being full of concretionary nodules, so firmly embedded in the matrix as frequently to be quite inseparable from it. This rock develops rough separation planes in certain stages of weathering. When broken across the cleavage planes in this state, and viewed edge-on, a wavy structure, caused by the lense-shaped bodies (nodules), of which it is in large part composed, is apparent. Viewed side-on it presents an undulatory or mammillated surface. These characteristics are unmistakable, as are also the following, and both are important to note. The gritty bands of rock above referred to, and on which the phosphate deposit in large part reposes unconformably, fractures rectangularly into lumps of the size of dice and upwards. On exposed surfaces these are seen *in situ*, and also in the northern creeks' channels, both loose and cemented together by oxide of iron, oxide of manganese, carbonate of lime, and phosphate of lime, as a breccia (conglomerate).

It is a notable fact that the rock phosphate itself bears the same features as does the mammillated limestone and the brecciated gritty rock in many places, and it is evident that a rearrangement of the molecules and a corresponding alteration in the mineral characteristics of the surface of the Cambrian rocks has taken place, the original form, however, remaining unchanged; in other words, we have here an instance of paramorphism on a large scale. The depth to which the chemical change has taken place has been regulated by the permeability of the rock to which the phosphatic solutions had access. Boulders of hard limestone rock and surfaces of the same rock *in situ* occur surrounded and also covered with rock phosphate that are scarcely affected at all, while in other places the whole surface of the Cambrian rocks has been

phosphatised. Adverting to the phosphoric acid contents of the altered portions, there occurred to me no evidence to lead one to conclude that any band in the Cambrian series had supplied the necessary phosphoric acid, and can only conclude that it was supplied from some other source. The concretions in the limestone bands has already been referred to. It occurred to me that these might have had a coprolitic origin. (Phosphatic concretions are also known to develop themselves on the sea floor, as pointed out by Mr. John Murray in a recent paper on deep sea deposits in the *Geographical Journal.)* Viewing the deposit as a whole, it may be inferred that where the conditions were most favorable for a good supply of phosphoric acid, and the rock was permeable and retained it, there the rock phosphate will be found in greatest quantity and purest quality.

The rock phosphate formation, which, as we have seen, spreads itself over and reposes unconformably on Cambrian rocks, is, in part, made up of the decomposed surface of those rocks *in situ*. This partially, or wholly, decomposed material retains its form of layers, and these layers conform to the bedrock layers. A large portion of the formation is also made up of derived material. At Baker's Gully layers of the parent rock are phosphatised. The derived material also assumes a rude stratification (that conforms to the surface of the older rock, as already remarked), and consists of soft and indurated clay of various colors, the clay sometimes containing a little grit in it; also calcareous marl, &c. Lumps and masses of rock phosphate of various shapes occur irregularly distributed through this formation. Sufficient exploratory work has not yet been done to enable one to make even a rough calculation of the quantity and quality of phosphate rock that may be expected in these beds, and the same remark will apply to the phosphatised Cambrian rock below. The "derived" portion of the phosphate deposit varies much in appearance, as it is likely to do in the quantity and quality of the phosphate rock it will carry; *e.g.*, at the ironstone quarries, where the bone phosphate was first discovered, a preponderating proportion of ferruginous clay, clay-grit, &c., carrying considerable quantities of ironstone through the mass, exists with but little visible rock phosphate. It is possible that in such a locality phosphate rock may underlie a heavy overburden. Payable rock is not likely to be found evenly distributed all over the area occupied by the phosphate formation; it is more probable that it may occur in irregular masses on different layers occupying the old channels of percolation. The masses may be disposed at any angle; also occur in concretionary nodules embedded in clayey material, either down on bedrock or be actually the bedrock itself—in short, anywhere through the formation.

A reference to the accompanying map and sections will illustrate the shape of the deposit, the way it outcrops, and also the portions that are without overburden. Except where channels of percolation existed in the bedrock the phosphate rock is not likely to be found at any great depth below the surface, but along lines of faults, and where earth movements brecciated the bedrock the depth to which it may reach is uncertain, but it is fair to infer that in such places phosphate rock will extend

downwards for some distance. In the valleys where the principal workings are situated it is probable that considerable bodies will be found, and in places on the sides and tops of the ridges there is reason to expect considerable quantities of rock phosphate. In many places the bedrock will be rock phosphate, as already explained. In the workings evidences are not wanting to show that between the clay and earthy material and the Cambrian limestone the phosphatic solutions found channels for percolation. In some of these channels oxide of iron is seen to occupy the place in contact with the limestone, and the phosphate rock forms a band next nearest to that. Concretionary, scoriaceous, and honey-combed ironstone blocks and lumps occur in the phosphate deposit. Near to and at the surface are fragments of ironstone, also scoriaceous and honey-combed fragments of impure magnesite, with veinings of flint-like material which probably is a hydrous silicate of alumina. It is a question as to in how far this is connected with the hydrous phosphate of alumina which occurs here. The magnesite and iron fragments, as also the loose lumps of rock phosphate, are useful, as they indicate the boundaries of the deposit.

The soil derived from the deposit is a rich dark-brown loam, and, as I was informed, these spots are distinguished by an early and rich crop of grass. Magnesite, gypsum, and oxide of manganese occur in the formation as well as iron. The experience of those who have worked the ground is that the rock phosphate derived from the upper portions in the workings contains a higher percentage of iron and alumina than that below, but that this will not hold good in every case. Mr. H. Y. L. Brown found that his more arenaceous samples contained hydrous phosphate of alumina.

As to the rock phosphate itself: There is an overburden in certain places that may be troublesome and militate against the financial success of extracting the rock, but this cannot be known until the quality and quantity of rock phosphate the deposit will yield is proven. As it does not occur in one constant layer the determination of its actual value will necessitate a considerable amount of prospecting work. Where the overburden is thin, through the convenient way the rock occurs, viz., on the slopes of steep inclines, it can be cheaply quarried, and on the whole the deposit can be easily and cheaply worked. There is little doubt but that very large reserves of low-grade phosphate material are present. but whether large quantities of rock of high grade and suitable for making superphosphates will be forthcoming cannot be stated at present; a certain tonnage will be forthcoming no doubt. In any case there is ample to warrant the expenditure of a considerable sum of money in proving its worth, and if these operations are carried out with good judgment it is quite possible that the proceeds from rock won and sold will cover the cos of all the prospecting work.

The rock phosphate presents diversified appearance, and ranges from earthy to a dense compact rock. The colors observed were a bluish-grey, ash-grey, yellowish-grey, white-grey, grey, chalky, chesnut-brown, red-brown, terracotta red, light ochre yellow, light khaki or straw color,

lavender blue, &c. The pseudomorphus forms have already been described. The rock of highest grade is weighty, compact, close-grained, and dense, and somewhat resembles bone on fracture faces. Selected samples can hardly be distinguished from Christmas Island phosphate rock. Iron and manganese occur as a coating and may prove deceptive as seeming to indicate a larger percentage of impurities than is actually the case. Blocks of rock occur weighing over 1 ton. As the rock occurs also in lumps and nodules promiscuously through the formation in places, the whole mass will have to be sorted. The purer rock contains 70 per cent. to 75 per cent. and upwards of tricalcic phosphate, with between 3 per cent. and 6 per cent. of iron and alumina. It is probable that much of the rock and rock fragments, while unsuitable for making superphosphate, may be finely ground and used as a manure in its natural state, as is done in America and elsewhere. Phosphate rock has been exposed in several small workings (*vide* plan). Quarries known as Nos. 1, 2, and 3 have been opened on the northern end and at Baker's Gully on the south. Through the courtesy of Mr. Barton I am able to supply the following:—4 tons 10cwts. 3qrs. of rock assayed 61 per cent. of tricalcic phosphate, and 2·8 per cent. iron and alumin—this test parcel was was sent to Wallaroo; 49 tons 3cwts. 1qr. assayed 57·66 per cent. tricalcic phosphate, and 2·52 per cent. was deducted for excess of iron and alumina = 55·14 per cent. at 28s. 2d., £69 4s. 9d.; 49 tons 0cwt. 1qr. assayed 65·97 per cent. tricalcic phosphate at 30s. = £73 10s. —these two parcels were sold to the Port Adelaide Chemical Works. The first parcel came from Baker's Gully; the second and third from No. 2 and No. 3 quarries, Mr. Phillips being my informant. There is every probability of other phosphate deposits existing in this district, where similar conditions occur, but whether they will be found free from heavy overburden, of good quality, and of dimensions that will render it possible to work them at a profit is a question. On section 473E the writer found fragments of phosphate rock scattered about, but the quality was indifferent, and the layer from which the fragments were derived would not pay to work. On the authority of Mr. Phillips, fragments of rock phosphate have been picked up on section 405, which is situated some five miles north of the principal discovery. The Clinton deposit differs from most others in that it reposes on and has phosphatised a limestone of great geological age, viz., Cambrian. Most of the valuable phosphate deposits, as previously enumerated, occur in limestone formations of either Pliocene, Miocene, or Eocene age. The Cambrian limestone at Clinton would prove less receptive for the phosphatic solutions than younger limestones, and for this reason is not so likely to have been phosphatised to as great a depth as would have been the case had the limestone been younger and more permeable. It is possible that very rich pockets occur at Clinton, but the absence of any regularly-defined outcrops of rock phosphate around the margins of the formation, and also its habit of occurring in boulders and nodules, indicates that the phosphate rock is likely to occur irregularly, and in places may be absent altogether.

The deposit is small in comparison with many others, but its discovery is of the utmost importance to South Australia, and Australia generally, because it opens the possibility of other and larger deposits being found, and a systematic search made anywhere along the coastal districts where limestone beds occur may be attended with success. The ease with which phosphate rock may lie undiscovered is shown by the fact that the Clinton area has been under cultivation for several years, and during that time fragments of rock, unearthed by the plough, were mistaken for limestone.

Mr. H. Y. L. Brown, Government Geologist of South Australia, visited the discovery shortly before the writer, and as his report contains valuable information it now follows *in extenso* :—

"The localities where the discoveries have been made are on sections 348, 349, 350, 351, 356, and 357, hundred of Clinton. They extend from two and a half miles to three and a quarter miles northward from Port Clinton, on Gulf St. Vincent, which is the nearest shipping place.

"The phosphate rock has been opened up and quarried to a small extent at four places, which are known as Nos. 1, 2, and 3 quarries and Baker's Gully, and exposed by cuttings and shallow excavations at numerous other places for a distance, from north-east to south-west, of one and a quarter miles.

"The existence of phosphate beneath the soil is indicated by scattered fragments and blocks which have been upturned and brought to the surface by the plough at the time the land was under cultivation. Some of these fragments are white in color, whilst others are brown, yellow, and iron-stained; they are often associated with iron ore and manganese, fragments of which are also scattered on the surface; they are embedded with black earth, clay, loam, marl, &c., and occur in patches. The soil generally contains nodules and lumps of phosphate rock, beneath which lies the phosphate deposit *in situ*. This consists of soft yellow and grey clay, calcareous marl, and sandy clay, embedded in which are segregated, rounded, and bedded-like masses of phosphate rock.

"The rock presents considerable variety in appearance, being sometimes grey, white, and chalk-like, reticulated with thin veins of denser composition, and at others a compact yellow grey and reddish-colored rock, with cellular spaces of various sizes, causing the whole to have a brecciated appearance, and again compact and nodular. In places earthy manganese fills the cellular spaces, particularly in the case of the soft chalk-like rock, which is also stained with iron oxide.

"The deposit as a whole has no regular stratification, although here and there appear traces of stratification, which, however, are not persistent. The strata in which the deposits occur are Cambrian limestones. Walls of this Primary limestone are to be seen in some of the excavations. These are in some places vertical and in others inclined, but dip generally at a much higher angle than the dip of the limestone strata. From this and other facts relating to the exposed portion of the limestone rock, I am of opinion that at one time caves and fissures, varying in extent, were formed in the limestone rock, and that at a later period

these became filled with the phosphate deposit. With regard to the size of these caves and depressions, the evidence obtainable from the position of the outcrops of limestone points to them being large. At Baker's Gully, section 357, the surface soil has been removed for a distance from east to west of four or five chains, exposing the phosphate deposit beneath. The width between the limestone rock outcrops is about a quarter of a mile. At quarry No. 3, section 348, a vertical limestone wall is visible on the eastern side, and the deposit is not defined westward. At No. 1 quarry an inclined limestone wall is visible on the west side. Sufficient work has not yet been done to allow the surface area of the deposits to be ascertained; this can only be determined by a careful survey and the sinking of trial holes.

"The depth to which the deposits may extend is unknown; the present shallow quarries are not deep enough to yield evidence on this point. Judging by the apparent width of the cavities containing the deposits it is reasonable to suppose that in some places the depth will be considerable. The question is one that will have to be determined by actual experiment.

"No fossils have been found so far in the deposits, and their origin can only be conjectured at present. My investigations lead me to believe that the quantity of rock containing a sufficient percentage of phosphate of lime to render it of commercial value is very large, and the configuration of the country is most favorable to the opening of quarries whereby the rock can be raised cheaply and expeditiously, and shipments averaging 70 per cent. of tricalcic phosphate and less than 6 per cent. of iron and alumina could be easily selected. As a matter of course the grading and selection of the rock must be guided by systematic and frequent analyses made on the spot.

"With regard to the analyses made by Mr. Goyder, Government Analyst (a list of which is appended), it is to be noted that several of the more argillaceous samples were found to contain hydrous phosphate of alumina instead of phosphate of lime. This substance, Mr. Goyder states, would probably be as valuable after fine grinding as phosphate of lime, but is not suitable for the manufacture of superphosphate.

"I am informed by Messrs. Barton and Phillips—the former being the discoverer of these deposits—that three parcels, totalling 103 tons, of phosphate rock have been disposed of for treatment at Adelaide and Wallaroo, and the following are the selling weights and percentages of the parcels as given:—

No. 1—49 tons, averaging 58 per cent. phosphate and 7 per cent. alumina and iron

No. 2—50 tons, averaging 65 per cent. phosphate and 3 per cent. alumina and iron

No. 3—4½ tons, averaging 61 per cent. phosphate and 2 per cent. alumina and iron

As I have not seen the account sales I am unable to give any further information as to prices, &c.

"On section 405 (see list of analyses), five miles north of the main discovery, rock phosphate of lime can be picked up on the surface. This indicates the existence of a deposit here; but so far no work has been done.

"It is most probable that deposits of phosphate rock occur in other portions of this district when occupied by the Cambrian limestone.

"This discovery is important, not only to South Australia, but to the Commonwealth generally, inasmuch as up to the present no similar deposit so likely to prove of such great commercial value has been found on this continent.

"List of Analyses.

	Phosphoric Acid.	Equivalent of Tricalcic Phosphate.	Insoluble Matter.	Oxide of Iron and Alumina.	Loss on Ignition.	
	%		%			
1	32·94	71·90	7·59	6·26	3	Rock phosphate, soft ferruginous. Farthest north quarry; average across, 10ft.
2	32·68	71·24	11·15	3·1	2	Rock phosphate, compact, whitish. Baker's Gully
3	32·76	71·52	11·02	2·9	2	" soft. Bottom of No. 1 quarry
4	34·56	75·44	8·28	3·10	4	" compact, whitish
5	28·16	61·47	21·16	5·18	3	" silicious rock phosphate. No. 3 quarry
6	31·84	69·50	12:34	3·1	2	" compact, whitish. Baker's Gully
7	31·41	68·67	11·08	2·9	2	" soft. Baker's Gully
8	15·43	33·68	52·0	—	1	" surface stone. Section 405
9	14·43	31·50	59·4	—	2	" nodular
10	1·68	3·62	94·7	—	1	Ferruginous claystone, nodular
11	17·0	—	38·77	19·06	18	Soft yellow with dense streaks; hydrous phosphate of alumina and ferruginous claystone
12	18·94	—	21·9	—	31	Soft white with reticulated dense veins; hydrous phosphate of alumina and claystone. Farthest south trench
13	6·91	—	74·5	—	5	Claystone and hydrous phosphate of alumina. Farthest north quarry, lowest depth
14	12·92	—	51·5	—	6	Ferruginous claystone and hydrous phosphate of alumina. Baker's Gully
15	12·13	—	44·0	—	11	Ferruginous claystone and hydrous phosphate of alumina. Barton's flux quarry
16	22·88	—	29·35	—	21	Hydrous phosphate of alumina and claystone, cellular rock. Baker's Gully and south
17	19·81	—	25·15	24·04	20	Hydrous phosphate of alumina. Baker's Gully
18	8·62	18·0	59·0	—	7	Ferruginous claystone and hydrous phosphate of alumina

"Note.—The insoluble matter consists of silica and clay. Samples 1 to 9 contain fluorine in not more than the usual percentage; the remainder only contain a minute trace."

VI.—WINNING AND PREPARING PHOSPHATE ROCK FOR MARKET.

From the description given of the various deposits it will be seen that the phosphate rock is usually encumbered with an overburden of very variable thickness. This has to be removed so that the rock may be quarried; and ploughing and scooping, sometimes with steam power, is the usual method adopted. Hydraulicing is sometimes resorted to, both to quarry and cleanse the rock and to remove useless matter. Centrifugal pumps or dredges are used in river deposits, and where the rock phosphate lies under water the rock is recovered in a similar way to harbor dredging. Some companies in America prepare the rock for market in the following manner:—To separate the clay and useless material from the rock phosphate washing is resorted to, and if the rock occurs in lumps exceeding 2in. to 3in. in diameter it is crushed before washing. The washing is done in wooden boxes 30ft. long and 3ft. to 6ft. wide. One or two revolving shafts are fixed and mounted with spirally-arranged blades in these boxes, which discharge into rinsers, of wire cloth or punched sheet iron, in cylindrical form of various lengths and diameters, the mesh varying according to requirements from $\frac{1}{16}$in. to 2in. The rinsers revolve, and water under pressure is applied internally and externally. The rock is then passed over rubber belts, and as these move along the rock is picked over and then discharged into hoppers; it is then dried in kilns or cylinders. The whole machinery is best arranged in tandems, down hill, so that gravitation may assist the movement of the material. Once dried the rock is kept under cover until exported.

The whole of the rock phosphate from some deposits has to be prepared for market; others again yield rock sufficiently clean and of such high grade that supers. can be made from them at once; the latter, however, are the exception.

VII.—TABLES OF PRODUCTION AND VALUE OF PHOSPHATES.

The following table, taken from the 1901 volume of *Mineral Industry*, will give some idea of the magnitude of the phosphate industry in the United States of America, the production being in long tons:—

Year.	South Carolina.	Florida.	North Carolina.	Tennessee.	Other States.	Totals.	Value.	
							Total.	Per Ton.
							$	$
1896	382,068	498,400	7,418	49,047	439	939,372	2,812,116	3·00
1897	333,626	543,490	7,000	121,251	2,000	1,007,367	3,022,101	3·00
1898	434,273	546,881	2,200	272,191	2,100	1,257,645	4,355,025	3·46
1899	476,238	706,677	15,000	462,561	3,000	1,663,476	6,350,144	3·82
1900	414,034	642,321	17,500	450,856	3,000	1,527,711	5,375,956	3·52

The total exports of phosphate rock to Europe from United States of America in 1900 amounted to 620,070 long tons, valued at $5,217,946,

against 868,513 long tons ($6,778,820) in 1899. The exports of Florida high-grade rock were 348,556 long tons in 1900, against 444,675 long tons in the preceding year.

C. LeNeve Foster gives the world's production of phosphate rock in metric tons and dollars as follows:—

Year.	Algeria.		Belgium.		Canada.	
		$	Cubic Metres.	$		$
1894.....	64,260	230,888	371,776	879,300	6,224	41,166
1895.....	157,886	634,323	506,730	683,140	1,653	9,565
1896.....	165,738	500,905	297,470	537,320	517	3,420
1897.....	228,141	912,564	350,056	436,762	824	3,984
1898.....	269,500	1,078,000	156,920	303,230	665	3,665
1899.....	324,983	1,299,932	190,090	342,180	2,722	18,000

Year.	France.		Norway.		Redonda, British W. Indies. *d*	
		$		$		$
1894.....	539,000	3,311,142	2,086	36,460	579	5,525
1895.....	526,784	3,160,600	1,601	23,760	5,778	24,880
1896.....	582,667	3,502,027	1,106	17,280	—	—
1897.....	535,390	2,852,887	*c* 872	12,960	812	5,525
1898.....	568,558	3,115,958	3,593	53,352	750	4,725
1899.....	645,868	3,334,145	— *e*	— *e*	— *e*	— *e*

Year.	Russia. *b*		Spain.		United Kingdom.		United States.	
		$		$		$		$
1894	14,072	31,680	40	80	711	6,385	1,098,147	3,296,602
1895	6,327	18,682	1,040	2,081	2,540	21,875	1,116,247	3,296,004
1896	3,776	11,065	770	3,080	3,048	26,250	952,370	2,812,116
1897	5,917	22,132	2,084	16,672	2,032	17,500	1,023,485	3,022,101
1898	— *e*	— *e*	4,500	46,003	1,575	13,565	1,257,645	4,355,025
1899	— *e*	— *e*	3,510	35,100	1,469	12,645	1,063,476	6,350,144

b Phosphorites exported. *c* Apatite exported. *d* Aluminium phosphate exported.
e Statistics not yet published.

VIII.—THE COMMERCIAL ASPECT OF PHOSPHATES AND SUPERS.

The thickness or depth of strata, its horizontal extension, accessibility, and conveniences for winning the rock, taken together with the percentage of tricalcic phosphate it carries (not less than 50 per cent. to 60 per cent.), and its freedom from an excess of the oxides of iron and aluminium, taken together are the points to be considered in determining the value of a phosphate rock deposit. The usual method of testing the value is to put boreholes down over the area 100ft. apart, and if the results warrant it to then sink pits 10ft. by 5ft. at intervals 500ft. apart. Fifteen feet is the greatest depth boreholes are sunk on South Carolina, when if no

phosphate is encountered, other localities are tested. The value of a phosphate rock depends very largely on its suitability for making superphosphates therefrom. In the manufacture of superphosphates the phosphate is first ground to a fine powder; then mixed with sulphuric acid. The acid dissolves the phosphate, and two parts of the lime (which are combined with the phosphoric acid in the tricalcic form) are first set free and then combine with the sulphuric acid, making a hydrous and water-soluble phosphate, called a superphosphate, and a sulphate of lime, or gypsum. The reaction may be shown thus—

Tricalcic Phosphate.	Sulphuric Acid.	Gypsum.	Monocalcic Phosphate.

$$3CaO, P_2O_5 + 2(H_2O, SO_3) = 2(CaO, SO_3) + CaO, 2H_2O, P_2O_5$$

There is also what is known as a "dicalcic" or "reverted" form that is insoluble in water, but readily soluble in ammonium citrate, as well as "available" to the roots of plants ($2CaO, H_2O, P_2O_5$). There is a tendency in nature for the monocalcic form to revert to the dicalcic form, and again for the dicalcic to revert to the tricalcic. It is said that when a superphosphate contains too much iron and alumina the tendency to revert is much accentuated, and for this reason are regarded as deleterious ingredients.

The sulphuric acid molecules' action on the constituent molecules in an ordinary phosphate rock is clearly shown in the following equations, given by Wyatt:—

Tricalcic phosphate	$Ca_3P_2O_8$	$+ 2H_2SO_4$	$= 2CaSO_4$	$+ CaH_4P_2O_8$
Calcium carbonate	$CaCO_3$	$+ H_2SO_4$	$= CaSO_4$	$+ CO_2 + H_2O$
Aluminium phosphate	$(AlPO_4)_2$	$+ 3H_2SO_4$	$= Al_2(SO_4)_3$	$+ (H_3PO_4)_2$
Phosphate of iron	$(FePO_4)_2$	$+ 3H_2SO_4$	$= Fe_2(SO_4)_3$	$+ (H_3PO_4)_2$
Magnesium carbonate .. .	$MgCO_3$	$+ H_2SO_4$	$= MgSO_4$	$+ CO_2 + H_2O$
Fluoride of calcium	CaF_2	$+ H_2SO_4$	$= CaSO_4$	$+ 2HF$

In the preparation of superphosphate the percentage of phosphoric acid per ton of rock is reduced, roughly, by one-half, but the tonnage in superphosphate therefrom is about doubled by the sulphuric acid, water, &c., that is added in the making.

Superphosphates made from rock phosphate that carries a large quantity of iron and alumina have a tendency to revert, or become insoluble again; therefore the unit percentage of tricalcic phosphate is worth less in rock containing a good deal of these than rock containing only a little. Calcium fluoride in excess also reduces the value of a rock phosphate, as it uses up too much acid; it forms sulphate of lime (gypsum) and adds weight, to the detriment of the superphosphate. Siliceous matter is a useless, harmless ingredient, adding unnecessary weight.

Phosphates carrying too much carbonate of lime are not good for making superphosphate, as they absorb too much acid. Some water must be added to form gypsum in the preparation of superphosphate. Some phosphates carry too little carbonate of lime. Tricalcic phosphate contains 45·81 parts by weight of phosphoric acid and 54·19 of calcic oxide. Iron, alumina, and magnesia may partially replace the lime in the raw

rock, but the phosphate is always deteriorated thereby, particularly when iron and alumina are the replacing constituents. Wyatt states that next to insufficiency of phosphoric acid itself, a lack of *carbonate* of lime (not lime) is the most serious defect in a phosphate. The defect is augmented in the presence of iron and alumina in any form. By blending, the happy quantity of carbonate of lime can often be effected. Finely-powdered chalk will do, or any other source of cheap carbonate of lime. This method of drying (viz., by adding lime) is to be preferred to any roasting process: how could it (says Wyatt) when we know that the monocalcic or water-soluble phosphate of lime cannot exist in any other form than the hydrated state? Iron and alumina are not so obstructive if carbonate of lime is present in proper quantity. Calcining the rock before treating is harmful. Free lime retards the drying action, and of course calcining produces free lime by driving off the carbonic acid (treating carbonates with acids also releases the carbon dioxide); hence it follows that a phosphate rock from which super. is to be made should be completely chemically analysed, and not only the percentage of tricalcic phosphate and of iron and alumina determined. Phosphates from different localities are often mixed to get a good rock for high-grade super. Finest grinding of the material is absolutely essential.

The factor for converting phosphoric anhydride (P_2O_5) into phosphate of lime is 2·18; consequently $2·26 \times 2·18 = 4·92$ phosphate of lime.

For traders the following form may be found useful in buying:— "The unit per ton of $Ca_3P_2O_8$ not to be less than ( ) and contain not more than ( ) per cent. of Fe and Al, calculated as oxides, on the dry basis. Every unit of these oxides, singly or combined, in excess of maximum shall be deemed to neutralise two units of the phosphate of lime, and such excess shall, therefore, be deducted from the total phosphate of lime if found in the results of chemical analysis."

In commerce phosphoric anhydride (P_2O_5) is misleadingly referred to as phosphoric acid. Laboratory tests show that the phosphoric acid in bone, while insoluble in water, may be partly dissolved at a certain temperature by a neutral solution of ammonium citrate. This medium is used to determine what is called "available" in other phosphatic products. The rate of solubility in this medium is measured by the method of preparation of the bone and its fineness, the phosphate in a raw bonemeal of the same fineness showing rather a lower rate of solubility than the phosphates in steamed bone. The phosphate in finest steamed bone is much more soluble than that of the coarser grades. This measure of the rate of solubility of bone, while not, perhaps, showing the exact rate at which the plants may obtain it, is a fairly safe guide in its use for most crops, as compared with those mineral phosphates which are not perceptibly soluble in this medium. The range of solubility in different kinds and grades of bone is from 20 per cent. to 75 per cent., and the average of a large number show that about 30 per cent. is soluble in citrate of ammonia, which would be called "available" if found in mixed fertilisers, and probably can be as safely depended upon as the "available" shown in other products.

Soluble Superphosphate means the percentage of tricalcic phosphate which has been dissolved, and *not* the percentage of monocalcic phosphate. In analysis terms: monocalcic phosphate of 17·3 per cent. is equal to tricalcic phosphate rendered "soluble," 27·2 per cent.; this means that it would require 27·2 per cent. tricalcic phosphate to furnish 17·3 per cent. of soluble phosphate. The former is called "soluble phosphate," and such a super. as the above would be described as containing 27·2 per cent. of soluble phosphate. In commercial transactions in mineral phosphates the "total available" only is regarded, the contents of insoluble being ignored.

Marketable superphosphate usually contains from 32 per cent. to 35 per cent. of bone phosphate, which contains some 17 per cent. of phosphoric acid, the phosphoric acid being in an "available" form. Bone ash superphosphates contain on the average about 16 per cent. of total available phosphoric acid. South Carolina rock superphosphates contain 12 per cent. to 14 per cent. of total available, of which 1 per cent. to 3 per cent. is dicalcic or reverted. The sum of the soluble and reverted forms is called the "total available."

Forida superphosphates, from the pebble rock, often contain 16 per cent. or 17 per cent. of total available, with varying percentages of reverted and insoluble.

Tennessee superphosphates run up to 16 per cent. to 18 per cent. of "total available," and the concentrated or "double superphosphates" may contain as high as 45 per cent. of "available," practically all of which is soluble. It will thus be seen that bone phosphate (raw) of 60 per cent. and upwards will, when treated, produce a superphosphate containing a 30 per cent. and upwards bone phosphate, the half of which should be soluble in water, and the other half in ammonium citrate. The phosphoric acid contents of a 60 per cent. (or any other percentage) raw rock may be ascertained by multiplying the 60 per cent. by 46 per cent., that being the proportion of phosphoric acid in bone phosphate.

The phosphates mentioned above, with the exception of Thomas phosphate, constitute what are known as "raw materials." As a rule they are not used directly on the land, but are first subjected to chemical treatment to render the phosphoric acid constituent more soluble and assimilable by the plant. In the raw state, even if ground very fine, the bone phosphate is insoluble in water, and the phosphoric acid is not so readily available to the plant as when "treated," on account of the slow rate of decay of the raw material. The finer the grinding of course the more rapid the decay, and this is the method adopted with phosphates that do not lend themselves readily to the manufacture of superphosphates, *e.g.*, when they have an excess of impurities such as alumina or iron, or the percentage of phosphoric acid is too low. Natural bones contain on an average about 20 per cent. of phosphoric acid (if good), which is equivalent to 43·60 per cent. of bone phosphate, but in certain cases 60 per cent. Ground bones are more readily attacked by the natural solvents—air, water, and solvent substances in the soil—than the mineral phosphates, but if the bones are "treated" the phosphoric acid contents become immediately available.

IX.—THE USES OF MINERAL FERTILISERS.

It is only within comparatively recent years that the uses of mineral fertilisers have been generally appreciated. There can scarcely be two opinions as to the value of good farmyard manure, for the mechanical and chemical effects combined can hardly be equalled, and there are cases where better results can be obtained with this than with any other manure. It is, however, rarely that well-balanced soils are found—soils that naturally contain the essentials for plant life in proper proportion. Most lack the proper proportion of some essential substance for certain plants; hence the great advantage to the farmer to have a thorough knowledge of the chemistry of his soil, and of the requirements of the plants he grows. These are essential to produce the best results. Some soils lack lime, others potash, while most can do with more phosphoric acid and nitrogen. A careful inspection of the rocks from which the soil covering any specific area was derived will afford a good idea of the substances of which the soil is composed.

For supplying essential deficiencies in soils there is nothing to equal mineral fertilisers. They can be had in such quantity, and in such a convenient form for distribution over the land, that the best possible results are obtainable at a minimum of cost. Voorhees suggests a practical method for discovering the deficiency in soils, and at the same time the manure that will produce the best results on the different plants. Take ten experimental plots, one-twentieth of an acre area, and sow in each plot a variety of plants: —

Plot	I.—Check	No fertiliser.
"	II.—Nitrate of soda	8lbs.
"	III.—Super.....	16lbs.
"	IV.—Muriate of potash	8lbs.
"	V.—Check.....	No fertiliser.
"	VI.—Nitrate of soda	20lbs.; super., 16lbs.
"	VII.— " "	20lbs.; potash, 8lbs.
"	VIII.—Phosphoric acid.....	40lbs.; potash, 8lbs.
"	IX.—Nitrate of soda	8lbs.; super., 16lbs.; potash, 8lbs.
"	X.—Check.....	No fertiliser.

Nitrogenous Manures, such as sulphate of ammonia, nitrate of soda, fowl manure, and guano, are stimulating and leaf-producing, and may be used beneficially with all plant life in moderation, especially market garden crops. Peas, clover, beans, and sainfoin are more benefited by potash and phosphate rather than nitrogenous manures.

Potash Manures, such as kainit (which contains sulphates and chlorides of potash in combination with sulphates and chlorides of sodium and magnesium), wood ashes, sulphate of potash, and nitrate of potash, are especially good for beans, peas, sainfoin, clover, cereals, potatoes, beets, and cabbages. They should be dug into the soil.

Phosphatic Manures, such as superphosphates and pure bonedust, without smell, are good for all plant life.

The quantity and kind of manure to use depends so largely on the character of the soil that, in a work of such small compass as this is,

recommendations that would be of value are not possible. There is no better method of ascertaining which is the manure or manures to use than a systematic practical test.

Potash is an essential to fruit trees and fruits. Voorhees states that more than 50 per cent. of the ash of fruits such as apples, cherries, pears, and plums is potash. Potash forms the base of the well-known fruit acids. Phosphoric acid is also essential to nourish the tree, but it is of less importance here than for cereals. Lime also is important with stone fruits, as also with others; cherries like limy soils. Citrus fruits like potash, and not too much nitrogen. Grapes like phosphates and potash, &c., &c. The groundwork of the whole thing lies in understanding the composition of the soil and the requirements of the plant, and no one rule (except in very general terms) will meet the requirements of every locality.

The usefulness of applications of lime and gypsum to certain soils has long been recognised. Lime in the carbonated form, if finely pulverised, is better for loaming light lands than the caustic lime (slaked lime), while for heavy lands the caustic is preferable to the carbonated. One writer states that nitrogen has a beneficial effect on wheat, rye, oats, barley, meadow grass, and beet crops; phosphoric acid on turnips, swedes, Indian corn (maize), sorghum, and sugarcane; and potash on peas, beans, clover, vetches, flax, and potatoes.

Sandy soils require lots of manure, because their porosity permits them to absorb such an abundance of oxygen that all their organic matter is rapidly burnt up. Clayey soils with more than 50 per cent. of pure clay are onerous to work and unprofitable to cultivate. If, however, 2 per cent. of burnt lime be added to such a soil it will entirely change its nature and consistency by transforming the silicate of alumina into a porous silicate and aluminate of lime. Clay lands with permeable subsoil in hot countries retain all the precious elements supplied to them for successive crops; with about 10 per cent. of carbonate of lime or chalk, they are the best of soils for wheat, corn, clover, hemp, beans, and peas. Pure lime never exists in the soil (being such a strong base) unless combined with carbonic, silicic, or sometimes with sulphuric and nitric acids.

X.—HINTS ON BUYING FERTILISERS.

The following information is condensed from Voorhees' work :—

To discover the nitrogen contents in ammonia—Multiply by 82 per cent. or divide by 1·214, because ammonia is 82 per cent. nitrogen, or because one part of the nitrogen is equal to 1·214 parts of ammonia.

Bone phosphate contains 46 per cent. actual phosphoric acid; hence, multiply the bone phosphate by 46 per cent., and the percentage of actual phosphoric acid is obtained.

Sulphate of potash is 54 per cent., the muriate of potash is 63 per cent. "actual" or potassium oxide respectively; hence, to convert the percentages of these forms into their equivalents of "actual," they are multiplied by the factors given.

When nitrate of soda contains 95 per cent. to 97 per cent. of pure nitrate, it means that it is 95 per cent. to 97 per cent. pure salt, and not

absolutely pure; hence the minimum percentage is 16·65 per cent., or 95 per cent. of 16·47 per cent., the percentage or pounds per hundred of nitrogen contained in pure nitrate of soda.

When muriate of potash is guaranteed 80 per cent. muriate, it means that 80 per cent. of the salt consists of pure muriate of potash; and because pure muriate of potash contains 63 per cent. of actual potash, or potassium oxide, the actual content of potash is derived by multiplying the 63 per cent., which the pure salt contains, by 80 per cent., and the result, 50·5 per cent., represents the amount of actual potash guaranteed.

The percentage of actual potash is found by multiplying 54 per cent. by 98 per cent. (or any other percentage given), since pure sulphate of potash contains 54 per cent. of actual potash.

Mixed fertilisers are sold on two lines. The following examples will be made clear by the above:—

No. 1.—(A) *Guarantee Basis of Equivalents in Combination.*

Nitrogen (equivalent to ammonia)	3·4 per cent.
Available phosphoric acid (equivalent to bone phosphate of lime)	18·22 "
Potash (equivalent to sulphate of potash)	10·12 "

Or, (B) *Guarantee on Basis of Actual Contents.*

Nitrogen (total)	2·50 per cent. to 3·25 per cent.
Phosphoric acid (available)	8·00 " to 10·00 "
Potash (actual)	5·50 " to 6·50 "

No. 2.—(C) *Buying on Unit Basis.*

A unit means 1 per cent. on the basis of a ton or 20lbs. A unit of phosphoric acid means 20lbs., and a quotation of $1 per unit equals a quotation of 5c. per pound. By this method both buyer and seller know exactly what they are doing.

(D) *Buying on the Ton Basis.*

The product is accompanied by a guarantee in this case, indicating the minimum amount of the constituents contained in the mineral.

When the value per unit or per pound of nitrogen, phosphoric acid, and potash are known and their percentages are given the value of different mixtures can be easily reckoned, and by simple calculation their relative values ascertained, *e.g.*—

No. 1 Mixture.

			Lbs. per Ton.		Cents per Lb.	
Nitrogen	1 per cent. × 20	=	20	at	30	= $6·00
Phosphoric acid (available)	6 " × 20	=	120	"	10	= 12·00
Potash	1 " × 20	=	20	"	10	= 2·00
						$20·00

No. 2 Mixture.

				Lbs. per Ton.		Cents per Lb.	
Nitrogen	4 per cent.	× 20	=	80	at	15	= $12·00
Phosphoric acid (available)	8 "	× 20	=	160	"	5	= 8·00
Potash	2 "	× 20	=	40	"	5	= 2·00
							$22·00

In reality the fertiliser at $22 per ton is cheaper than the one at $20 per ton.

Cost per pound of constituents in—

	No. 1.		No. 2.
Nitrogen	$0·30	..	$0·15
Phosphoric acid (available)	0·10	..	0·05
Potash	0·10	..	0·05

The purchaser should note how the certificated contents of a manure are stated, and calculate the equivalents into the "actual" contents. Manufacturers and dealers in fertilisers should be compelled to state the amount of the different constituents contained in their products, as well as sources of supply.

To convert the guarantee of—

Ammonia	into	Nitrogen	× by	0·8235
Nitrogen	"	Ammonia	× "	1·214
Nitrate of soda	"	Nitrogen	× "	0·1647
Bone phosphate	"	Phosphoric acid	× "	0·458
Phosphoric acid	"	Bone phosphate	× "	2·183
Muriate of potash	"	Actual potash	× "	0·632
Actual potash	"	Muriate of potash	× "	1·583
Sulphate of potash	"	Actual potash	× "	0·54
Actual potash	"	Sulphate of potash	× "	1·85

A complete chemical analysis of a fertiliser indicates very clearly the source of the materials by the form in which the constituents exist in the mixture; *e.g.*, if chlorine is high the potash contents will probably have been derived from kainit or muriate; if low, probably from a high-grade sulphate. If in the case of phosphoric acid it is shown that of every 100lbs. of the total 80lbs. are soluble, 10lbs. reverted, or $\frac{2}{10}$ of the whole is "available," 10lbs. of every 100lbs. only are insoluble, which is not only an indication, but a positive proof, that the phosphoric acid is derived from a superphosphate.

Schedule of Trade Values adopted by Experimental Stations, for 1898, in United States of America.

	Cents per Lb.
Nitrogen as nitrates	13·0
Nitrogen as ammonia salts	14·0
Organic nitrogen, in dried and fine-ground fish, meat, and blood, and in mixed fertilisers	14·0
Organic nitrogen, in fine-ground bone and tankage (finer than 1·50 inch)	13·5
Organic nitrogen, in coarse bone and tankage (coarser than 1·50in.)	10·0
Phosphoric acid, soluble in water	4·5
Phosphoric acid, soluble in ammonium citrate (In New Jersey the price for the "soluble" and "reverted" is identical, viz., 4·5c., owing to the different methods used in the determination of the "reverted")	4·0

SCHEDULE OF TRADE VALUES—*continued.*

	Cents per Lb.
Phosphoric acid, insoluble, in fine bone and tankage (finer than 1·50in.)	4·0
Phosphoric acid, insoluble, in coarse bone and tankage (coarser than 1·50in.)	3·5
Phosphoric acid, insoluble, in mixed fertilisers	2·0
Phosphoric acid, insoluble, in fine-ground fish, cotton-seed, meal, castor pomace, and wood ashes	4·0
Potash as muriate	4·25
Potash as sulphate, and in forms free from muriates (or chlorides)	5·0

The commercial valuations do not necessarily indicate the agricultural value of a fertiliser, for obvious reasons.

XI.—TEST FOR PHOSPHORIC ACID (PHOSPHORUS).

Rhead and Sexton, in their work on "Assaying and Metallurgical Analysis," p. 356, give the following method, amongst others, for testing for phosphorus, by which the phosphoric acid in rock phosphate is precipitated by ammonium molybdate:—"The addition of ammonium molybdate to a solution containing phosphoric acid acidified with nitric acid, precipitates, on warming, a heavy golden-yellow precipitate, consisting of phospho-molybdate of ammonia, having a composition $(NH_4)_3 11MoO_3PO_4 6H_2O$, insoluble in dilute nitric acid, and containing only 1·63 per cent. of phosphorus. This precipitate may be dried at 100° C. without alteration."

"The ammonium molybdate solution may be prepared by dissolving 40grms. of powdered ammonium molybdate in hot water and diluting to 500c.c., and filtering, if necessary.

"Any arsenic acid present is also thrown down, since it behaves like phosphoric acid"; but it is unlikely that arsenic will trouble the rock phosphate prospector.

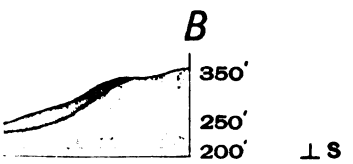
If the rock be a common limestone, or contains much carbonate of lime, it will effervesce to a considerable extent when the nitric acid is added.

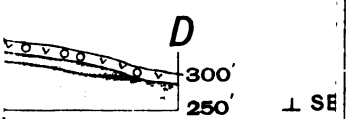
The most expeditious field test is—Moisten a spot on the rock sample with nitric acid, then sprinkle a tiny particle of powdered ammonium molybdate on the acid, when, if the rock contains phosphorus, the white powder will immediately turn yellow. When the rock absorbs the nitric acid too rapidly to moisten the powder, put another drop on the powder.

Phosphates held with clean platinum forceps in the non-luminous flame of the blowpipe give a yellowish-green coloring to the flame if first moistened with sulphuric acid.

If *Gypsum* is heated to not exceeding 260° C. the combined water in its constitution is expelled. If then ground fine and moistened it will set hard by taking up its lost water. If overheated in the process the experiment will be spoilt. Gypsum, if pure, does not effervesce with acids, but limestone does. Is soluble in hydrochloric acid and also in 400 to 500 parts of water. Colors the B.B. flame reddish-yellow.

-*Nos. are in feet abo*





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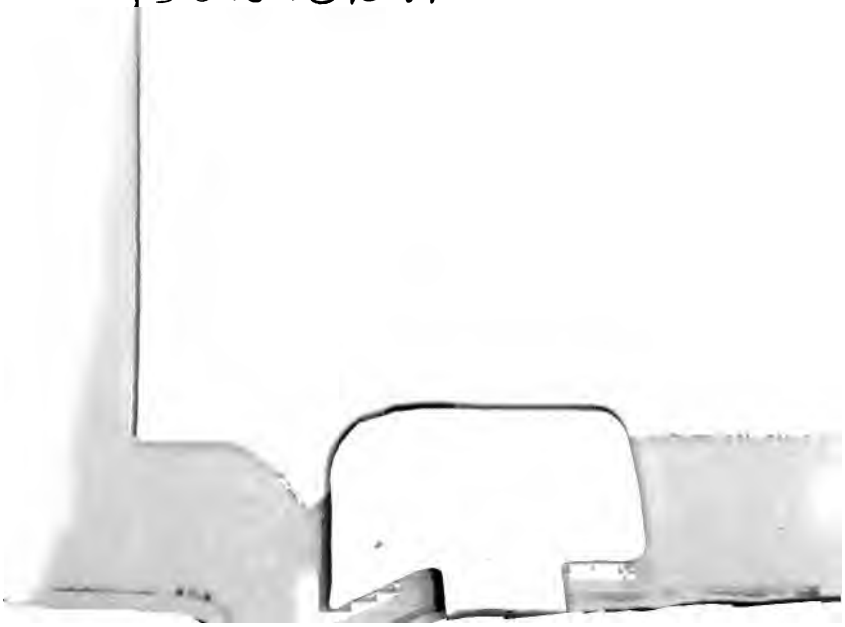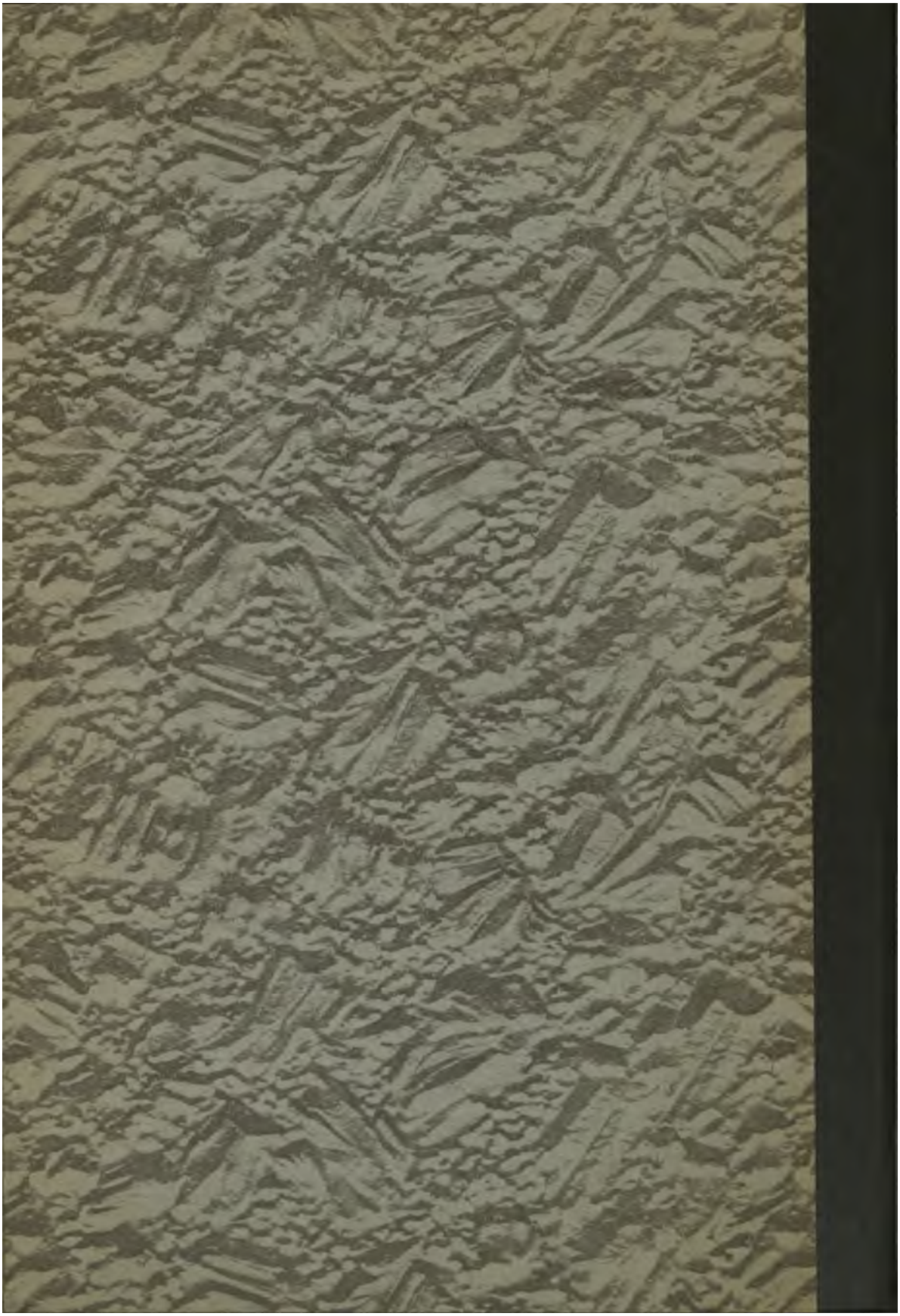
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